

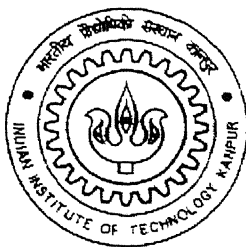
# Prediction of Vapor-Liquid Equilibrium Data for Refrigerant Mixtures

*A Thesis submitted  
in partial fulfilment of the requirements  
for the degree of*

**Master of Technology**

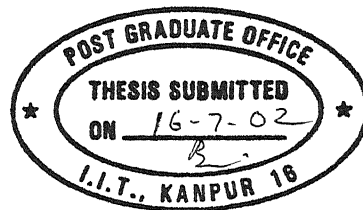
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July 2002



## CERTIFICATE

This is to certify that the work contained in the thesis entitled "**Prediction of Vapor-Liquid Equilibrium Data for Refrigerant Mixtures**" has been carried out by *Padamata Srinivas Rao* under my supervision and that this work has not been submitted elsewhere for a degree.

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## Abstract

An ever-increasing concern on the stratosphere ozone depletion has led to a worldwide ban on ChloroFluoroCarbons (CFCs) and prompted rigorous search for alternative refrigerants with zero Ozone-Depletion Potential (ODP) and lower Global Warming Potential (GWP). The prediction of phase equilibrium behavior of complex mixtures over broad ranges of temperature and pressure is an important problem in chemical process design. The objective of the present work is to predict and compare the VLE data for refrigerant mixtures using the following three different models (1) UNIFAC Method, (2) modified UNIFAC Method and (3) Peng-Robinson model with van der Waal one fluid-mixing rule.

A total of thirty-one binary mixtures of different classes, have been studied using the above three models and the predicted results are compared with experimental data. It was found that the UNIFAC model is able to predict the VLE data much better than the other two models.

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# Nomenclature

## Alphabets

$A_{ij}$	Three suffix Margules parameter
$A_{ij}$	Van Laar parameter
$a$	Parameter in Equation of state
$a_{nm}$	UNIFAC group interaction parameter between groups n and m
$b_{nm}$	UNIFAC group interaction parameter between groups n and m
$c_{nm}$	UNIFAC group interaction parameter between groups n and m
$a_{ij}$	Cross term of energy parameter $a$ in mixing rules
$B, B'$	Second Virial coefficient
$b_{ij}$	Cross term of volume parameter $b$ in mixing rules
$C, C'$	Third Virial coefficient
$F_i$	Auxiliary property for component I (surface fraction/mole fraction)
$f$	Fugacity
$f$	Fugacity of component $i$ in the mixture
$G_{ij}$	NRTL parameter
$g$	Molar Gibbs free energy
$g^E$	Molar excess Gibbs free energy
$\bar{g}^E$	Partial Molar Gibbs free energy
$g_{ij}$	Energy parameter in NRTL equation
$k_{ij}, k_{ji}$	Binary interaction parameters
$K_i$	Equilibrium constant
$l_{ij}$	Binary interaction parameter
$n$	Number of moles
$N$	Number of data points
$P$	Pressure
$Q_k$	Group area parameter

$q_1, q_2$	Measure of volume of component
$q$	Surface area parameter
$R$	Universal gas constant
$R_k$	Group volume parameter
$r_i$	Volume parameter of component $i$ in UNIQUAC
$S$	Function of acentric factor
$T$	Temperature
$u_{ij}$	Average interaction energy for the interaction of component $i$ with the component $j$
$u_{mn}$	Measure of interaction energy between groups $m$ and $n$
$V_i^*$	Auxiliary property of component $i$ (volume fraction / mole fraction)
$V_i^*$	Empirically modified $V_i$ -value.
$V$	Volume
$v$	Molar volume
$\bar{v}_i$	Partial molar volume of component $i$
$x_i$	Mole fraction of component $i$ in liquid phase
$y_i$	Mole fraction of component $i$ in vapor phase
$Z$	Compressibility factor
$z$	Co-ordination number
$z_1, z_2$	Volume fractions

## Greek letters

$\alpha$	Temperature dependence of parameter $a$
$\alpha_{ij}$	Non-randomness parameter in NRTL equation
$\Gamma_i$	Integration constant
$\Gamma_k$	Group residual activity coefficient
$\Gamma_k^i$	Residual activity coefficient of group $k$ in a reference solution containing only molecule of type $i$

$\gamma$	Activity coefficient
$\tau_{ij}$	NRTL parameter, UNIQUAC parameter
$\theta_i$	Area fraction of component $i$
$\Lambda_{ij}$	Wilson parameter
$\lambda_{ij}$	Energy parameter in Wilson equation
$\mu$	Chemical potential
$v_k^i$	Number of groups of type in a molecule of component $i$
$\phi$	Fugacity coefficient
$\phi_i$	Segment fraction of component $i$
$\phi_i$	Fugacity coefficient of component $i$ in mixture
$\psi_{mn}$	UNIFAC parameter
$\omega$	Acentric factor
$\Delta$	Average deviation

## Superscripts

$E$	Excess
$l$	Liquid phase
$o$	Reference state
$s$	Saturated
$v$	Vapor phase

## Subscripts

$c$	Critical property
$i, j$	Molecular species
$m$	mixtures
$r$	Reduced property
$t$	Total basis



## **CHAPTER 1**

# **INTRODUCTION**

The estimation of phase equilibrium behavior of complex mixtures over broad ranges of temperature and pressure is an important problem in chemical process design as most of the industrial chemical processes deal with operations such as, extraction, adsorption, distillation, leaching, and absorption, which involve phase contacting. In particular distillation is the most important separation and purification process used in chemical industry, where vapor and liquid phases co-exist. This requires the process designer to have a reliable Vapor-Liquid Equilibria (VLE) data, for design of distillation columns. Though for a large number of binary and for a few multi-component systems the experimental VLE data can be found in literature, the experimental data is not available at all desired conditions. This necessitates the designer either to experimentally determine or estimate the required VLE data. But if the process of interest is to be performed over a wide range of pressures and temperatures, the number of experimental points required becomes large. Hence the available experimental data can be used to develop a model, which in turn can be used to predict the data at the required operating conditions.

In accord with an increasing concern on the stratospheric ozone depletion, the timetable toward a complete ban on the production and consumption of ChloroFluorCarbons (CFCs) and HydroChloroFluorCarbons (HCFCs) has been accelerated to phase them out. The study of the 'ozone hole' above the Antarctic established the relationship between the chlorine and ozone content in the stratospheric zone and dictated that the chlorine oxide ( $\text{ClO}^\cdot$ ) radical is mainly responsible for the ozone destruction. This radical is formed by chlorine atoms released by chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), used mainly in the refrigeration industry. The environmental regulations that have been imposed on all countries in order to tackle the problem of ozone depletion, forced the refrigeration industry to totally phase out CFCs in 1995, and HCFCs in the following years (2015 for western Europe) (Clodic and sauer, 1994). The recommended worldwide ban on many

low-molar mass chlorofluorocarbons has prompted rigorous search for alternatives with zero Ozone-Depletion Potential (ODP) and lower Global Warming Potential (GWP).

The chlorofluorocarbons were primarily used as refrigerants, but are also important as blowing agents in polymer foam manufacture and cleaning solvents in electronic circuit manufacture. In many cases, such as refrigeration applications (which is most important area of use of CFC), it is necessary to develop alternative fluids with thermodynamics properties, which are similar to CFCs they are to replace so that existing equipment can be used with a minimum of modification. For this purpose first hydrocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) and their mixtures were suggested, though now fluorinated alcohols and their mixtures HFCs and HCFCs and other fluids are also being considered (Sauermann et al., 1993; Laugier et al., 1994; Nowaczyk and Steimle, 1992). The use of mixtures can result in energetic improvements, extensions of the applications, such as flammability, insolubility in oil or green house effect implications.

The available models for the prediction of VLE data can be broadly classified as activity coefficient models and Equation of State (EOS) models. In activity coefficient model the liquid phase non-ideality is described in terms of an activity coefficient ( $\gamma_i$ ) for component  $i$  of the system. The vapor phase non-ideality is expressed in terms of fugacity coefficient ( $\phi_i$ ) for component  $i$  of the system. The fugacity coefficient can be obtained by making use of an appropriate equation of state. Some of the models that belong to this method are Margules, Van laar, UNIFAC etc., (Rao Y. V. C. 1997). In EOS approach both the liquid and vapor phase non-idealities are explained by the fugacity coefficient where, it is indicated by  $(\phi_i)$  for the liquid phase and  $(\phi'_i)$  for the vapor phase. Some of the equations of state such as Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), Peng-Robinson-Stryjek-Vera (PRSV), Benedict-Webb-Rubin (BWR) are used in this method (Mark et al. 1991).

The activity coefficient models give satisfactory results at low to moderate pressures. However, their applications at critical and supercritical pressures yield inaccurate VLE data. EOS approach is a powerful tool for addressing this problem. The major advantage of the EOS approach is its applicability over a wide range of temperatures and pressures including critical and supercritical, where the activity coefficient models fail. In process

simulation calculations. the equations of state are widely used due to their algebraic simplicity and their accuracy.

There are two requirements for the equations of state to be successful. (1) The EOS must predict the saturation pressure of pure substances accurately. (2) The mixing rules must be available which correctly extend these equations to multicomponent mixtures. Different equations of state predict the thermodynamic properties with different degrees of accuracy and they require different types of data for proper evaluation. Hence, a reliable EOS for practical applications must be physically sound, reasonably simple and present no convergence problems.

Cubic equations of state, which are in wide use, model the repulsive forces incorrectly resulting in inaccuracies in representing the thermodynamic properties, especially in the supercritical fluid and condensed phase regions. Van der Waals proposed the first cubic equation of state in 1873. The well-documented van der Waals equation is the most influential EOS that incorporated both the repulsion and attraction of intermolecular forces in the expression. Numerous EOS have since been proposed within the framework of this concept (Anderko (1990)). Redlich and Kwong (1949) modified the attractive term of the expression of the van der Waals EOS, but retained its repulsive term, to satisfy the boundary conditions in the low and high-density limits. The Redlich-Kwong (RK) EOS is among the most fruitful of the van der Waals family for routine engineering calculations. Various modifications of the RK equation to improve its accuracy have also been suggested. These are represented by the Soave (1972) and the Peng and Robinson (1976) equations.

The extension of equations of state to describe phase behavior for a broad range of multicomponent mixtures had been more difficult due to limited applicability of the van der Waals (vdW) one-fluid mixing rules that are commonly used for relatively simple mixtures. The vdW mixing rules are incapable of representing the highly non-ideal mixture behavior of polar or associating fluids. Consequently, much effort in recent years has been devoted toward developing alternative mixing rules to extend the cubic equations of state to complex mixtures [Orbey and sandler (1996); Heidemann (1996)]. With the advent of multiparameter mixing rules, equations of state are now being used

for the phase equilibrium calculations of complex mixtures that were traditionally described with activity coefficient models.

The present work deals with prediction of VLE data for refrigerant mixtures using UNIFAC method. Modified UNIFAC and Peng-Robinson with Van der Waals one fluid mixing rule. The cubic equation has three roots. The identifications of these roots are very easy as. higher root correspondent to the vapor, low value corresponding to the liquid value and intermediate root has no significance. This makes the prediction of volume at different temperatures and pressures possible, by solving the compressibility equation of state in terms of the compressibility factor ( $Z$ ) or volume.

VLE calculations are done using UNIFAC, Modified UNIFAC and PR Equation for binary mixtures of refrigerants. Van der Waals one fluid mixing rule is used with EOS for the VLE calculations. The results are then compared with the available experimental data.

Chapter#2 lays emphasis on the important models that are used for VLE calculations in the two available approaches. Chapter 3 focuses on literature survey. In the next chapter development of the models with mixing rule and calculation procedure is discussed. Fifth chapter presents the results and a discussion of the results, followed by conclusions.

## CHAPTER 2

# THERMODYNAMIC MODELS

### 2.1 Equilibrium Criterion

For a closed system containing vapor and liquid phases, with each phase consisting of  $c$  components, in a state of equilibrium at a constant temperature ( $T$ ) and pressure ( $P$ ), the criterion for equilibrium is given by (Smith et al. 1996).

$$\mu_i^l = \mu_i^v \quad (i = 1, 2, \dots, c) \quad (2.1)$$

where,  $\mu_i^l$  and  $\mu_i^v$  are chemical potentials of component  $i$  in liquid and vapor phases, respectively. The chemical potential  $\mu_i$  is given

$$\mu_i = \Gamma_i(T) + RT \ln f_i \quad (2.2)$$

where  $\Gamma_i(T)$ , an integration constant, is a function of temperature only and  $f_i$  is the fugacity of component  $i$  in the mixture. Using Eq. (2.2) in Eq. (2.1), the general criterion for vapor-liquid equilibrium reduces to

$$f_i^l = f_i^v \quad (i = 1, 2, \dots, c) \quad (2.3)$$

The Eq. (2.3) can be rewritten as (Rao Y. V. C. 1997).

$$\gamma_i x_i f_i^0 = \phi_i^v y_i P \quad (i = 1, 2, \dots, c) \quad (2.4)$$

where  $\gamma_i$  = activity coefficient of component  $i$  in the solution.

$x_i, y_i$  = mole fractions of component  $i$  in liquid and vapor phases, respectively.

$f_i^0$  = fugacity of component  $i$  in the standard state.

$\phi_i^v$  = fugacity coefficient of component  $i$  in the vapor phase.

$P$  = Pressure at which the system is held.

The standard state fugacity ( $f_i^0$ ) is the fugacity of component  $i$  at the mixture temperature and at some arbitrarily chosen pressure and composition. For most of the liquid solutions, the standard state for component  $i$  is chosen as the liquid phase of the

pure component  $i$  at the system temperature and pressure. With this choice of the standard state,  $f_i^0$  is given by.

$$f_i^0 = P_i^s \phi_i^s \exp \left\{ \frac{v_i^l (P - P_i^s)}{RT} \right\} \quad (2.5)$$

where,  $\phi_i^s$  is the fugacity coefficient of component  $i$  at saturation pressure  $P_i^s$  for the same component  $i$  at temperature  $T$ .  $v_i^l$  is the molar volume of liquid for component  $i$ . Substitution of Eq. (2.5) in Eq. (2.4) results in the *basic equation for vapor-liquid equilibrium*, which is given by

$$\gamma_i x_i P_i^s \phi_i^s \exp \left\{ \frac{v_i^l (P - P_i^s)}{RT} \right\} = \phi_i^v y_i P \quad (i = 1, 2, \dots, c) \quad (2.6)$$

At low pressures, the vapor phase can be assumed to behave like an ideal gas. Hence  $\phi_i^v = 1$  and  $\phi_i^s = 1$ . Moreover, the Poynting correction factor (exponential term in Eq. (2.6)) is approximately equal to unity. At moderate pressures  $\phi_i^v$  and  $\phi_i^s$  are approximately equal and hence it is reasonable to assume that  $(\phi_i^v / \phi_i^s) = 1$ . Thus at low to moderate pressures Eq. (2.6) reduces to

$$\gamma_i x_i P_i^s = y_i P \quad (1, 2, \dots, c) \quad (2.7)$$

$$\text{or} \quad \gamma_i = \frac{y_i P}{x_i P_i^s} \quad (1, 2, \dots, c) \quad (2.8)$$

However, at high pressures these assumptions are not valid. Eq (2.3) can also be written as

$$\phi_i^l x_i P = \phi_i^v y_i P \quad (\text{since } \phi_i = (f_i / y_i P))$$

$$\text{or} \quad \phi_i^l x_i = \phi_i^v y_i \quad (1, 2, \dots, c) \quad (2.9)$$

$$\text{or} \quad K_i = \frac{y_i}{x_i} = \frac{\phi_i^l}{\phi_i^v} \quad (1, 2, \dots, c) \quad (2.10)$$

where  $K_i$  is the  $K$  factor or equilibrium constant for component  $i$ .

The methods available for the prediction of VLE data can be broadly classified as:

1. Activity coefficient Approach
2. Equation of State (EOS) Approach

The main difference between the two methods lies in the reference state. For the EOS method, the reference state is the ideal gas condition and the fugacity coefficient is a measure of the deviation from this state for both the vapor and liquid phases. For activity coefficient methods, the reference state for the liquid is the pure liquid at the same temperature and pressure of the mixture. The choice of the thermodynamic model to be used depends on

- Nature of the components
- The pressure and temperature conditions

### ***NATURE OF THE COMPONENTS***

The nature of the component decides the extent of non-ideality. Non-ideality is due to the interaction between the molecules, which depends on intermolecular forces. This interaction is more evident in the liquid phase where the molecules are packed closer. The choice between the EOS method and Activity coefficient method can be made based on the polar nature of the components.

Hydrocarbons like ethane, propane, pentane are non-polar and can be represented adequately by EOS methods. Mixtures of polar compounds may be represented using Activity coefficient methods. Mixtures of polar and non-polar compounds can give rise to two immiscible liquid phases and hence a model that is capable of predicting a phase split must be considered. This would be an Activity Coefficient method like NRTL or UNIQUAC. Wilson or Van Laar models are incapable of predicting splitting of the liquid phase.

### ***TEMPERATURE AND PRESSURE***

At high pressures and at temperatures above critical, the activity coefficient models fail. EOS models are valid over a wide range of temperature and pressure. Since

consistency is inherent in the EOS approach, these are applicable even at the critical conditions.

## 2.2 Activity Coefficient Approach

The basis of activity coefficient approach is the activity, which is defined as

$$a_i = \frac{f_i(T, P, x_i)}{f_i^0(T, P^0, x_i^0)} \quad (2.11)$$

Here  $a_i$  is the activity of component  $i$  and  $f_i^0$  is the standard state fugacity (at some arbitrarily defined pressure  $P^0$  and some arbitrarily defined composition  $x_i^0$ ). The activity coefficient  $\gamma_i$  is defined as

$$\gamma_i = \frac{a_i}{x_i} = \frac{f_i}{x_i f_i^0} \quad (2.12)$$

The partial molar Gibbs free energy is given by

$$\mu_i - \mu_i^0 = \tilde{g}_{i,real} - \tilde{g}_{i,ideal} = \tilde{g}_i^E = RT \ln \frac{f_i^I}{f_{i,ideal}} \quad (2.13)$$

From Raoult's law one can obtain

$$f_{i,ideal} = x_i f_i^0 \quad (2.14)$$

$$\tilde{g}_i^E = RT \ln \frac{\gamma_i x_i f_i^0}{x_i f_i^0} = RT \ln \gamma_i \quad (2.15)$$

Using the definition of partial molar excess Gibbs free energy, one can obtain

$$\ln \gamma_i = \frac{1}{RT} \left[ \frac{\partial (n g^E)}{\partial n_i} \right]_{T, P, n_j} \quad (2.16)$$

where,  $g^E$  = molar excess Gibbs energy. The relation between  $g^E$  and the activity coefficients can also be expressed as

$$g^E = \sum_{i=1}^c x_i \tilde{g}_i^E = RT \sum_{i=1}^c x_i \ln \gamma_i \quad (2.17)$$

The Gibbs-Duhem relation for a binary mixture is given by

$$x_1 \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T, P} = x_2 \left( \frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T, P} \quad (2.18)$$



Assume that  $g^E$  can be expressed as a function of temperature, pressure and composition. That is,

$$g^E = f(T, P, x_i) \quad (2.19)$$

The Activity coefficient can then be derived from Eq. (2.16) and substituted into the following equilibrium constraint.

$$y_i P \phi_i^v = \gamma_i(T, P, x_i) x_i f_i^0 \quad (2.20)$$

The system of equations defined by Eq. (2.20) can be solved for the equilibrium temperature, pressure, and concentration. Therefore, the basis of activity coefficient approach is to find an accurate form of Eq. (2.19).

The commonly used Activity coefficient models are

- Margules Equation
- Van Laar Equation
- Wilson Equation
- NRTL Equation
- UNIQUAC Equation
- UNIFAC Equation
- MODIFIED UNIFAC Equation

### 2.2.1 Margules Equation

The Margules equations, can be deduced from the expressions for excess Gibbs free energy given by Wohl's expansion (Mark et al. 1991)

$$\frac{g^E}{RT(x_1 q_1 + x_2 q_2)} = 2a_{12}z_1z_2 + 3a_{112}z_1^2z_2 + 3a_{122}z_1z_2^2 + \dots \quad (2.21)$$

where

$$z_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2} = \text{the volume fraction of component } i \quad (2.22)$$

$q_i$  = measure of volume of the component  $i$ .  $a_{12}$ ,  $a_{112}$ ,  $a_{122}$  ... are empirical constants which signify two body, three body..... interactions.

Margules assumed the size of molecules to be equal ( $q_1 = q_2$ ). After some rearrangements Eq. (2.21) reduces to the Margules three suffix equation given by

$$\frac{g^E}{RT} = (A_{12}x_1 + A_{21}x_2)x_1x_2 \quad (2.23)$$

where  $A_{12}$  and  $A_{21}$  are adjustable parameters.

The activity coefficients  $\gamma_1$  and  $\gamma_2$  are given by

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2 \quad (2.24)$$

$$\ln \gamma_2 = [A_{21} + 2(A_{12} - A_{21})x_2]x_1^2 \quad (2.25)$$

The Margules three suffix equations are used for symmetrical systems ( $q_1 = q_2$ ) i.e. systems where all the components have almost equal size.

### 2.2.2 Van Laar Equation

Margules equation assumes equal size for molecules, which is not true. If the size difference of the molecules ( $q_1 \neq q_2$ ) is incorporated into Wohl's expansion, (Mark et al. 1991) it gives

$$\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1 + x_2q_2} \quad (2.26)$$

Simplifying Eq. (2.26) leads to van Laar equations, which are given by

$$\frac{g^E}{RT} = \frac{A_{12}A_{21}x_1x_2}{x_1A_{12} + x_2A_{21}} \quad (2.27)$$

$$\ln \gamma_1 = A_{12} \left[ \frac{A_{21}x_2}{x_1A_{12} + x_2A_{21}} \right]^2 \quad (2.28)$$

$$\ln \gamma_2 = A_{21} \left[ \frac{A_{12}x_1}{x_1A_{12} + x_2A_{21}} \right]^2 \quad (2.29)$$

where  $A_{12}$  and  $A_{21}$  are adjustable parameters.

### 2.2.3 Wilson Equation

For mixtures in which the components differ from each other in molecular size and interaction between the unlike and like molecules are different, Wilson (1964) proposed the following expression for the excess Gibbs free energy of a binary solution.

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \quad (2.30)$$

where  $\Lambda_{12}$  and  $\Lambda_{21}$  are two adjustable parameters, which are related to pure component molar volumes and characteristic energy differences.

$\Lambda_{12}$  and  $\Lambda_{21}$  are given by

$$\Lambda_{12} = \frac{v_2}{v_1} \exp \left[ -\frac{\lambda_{12} - \lambda_{11}}{RT} \right] \quad (2.31)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp \left[ -\frac{\lambda_{12} - \lambda_{22}}{RT} \right] \quad (2.32)$$

$v_i$  = molar volume of pure component  $i$ .

$\lambda_{ij}$  = energy of interaction between molecules of component  $i$  and  $j$ .

The activity coefficients can be derived from Equation (2.30) and are given by

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (2.33)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (2.34)$$

#### 2.2.4 Non-Random Two Liquid (NRTL) Equation

The Non-Random Two Liquid (NRTL) equation proposed by Renon and Prausnitz (1968) is applicable to partially miscible as well as completely miscible systems.

The NRTL equation for excess Gibbs free energy is given by

$$\frac{g^E}{RT} = x_1x_2 \left[ \frac{\tau_{21}G_{21}}{x_1 + G_{21}x_2} + \frac{\tau_{12}G_{12}}{x_2 + G_{12}x_1} \right] \quad (2.35)$$

where

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \quad (2.36)$$

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} \quad (2.37)$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \quad (2.38)$$

$$G_{21} = \exp(-\alpha_{21}\tau_{21}) \quad (2.39)$$

$g_{ij}$ =energy of interaction between molecules of component  $i$  and  $j$ .

The parameter  $\alpha_{12}$  is introduced to take into account the non-randomness of the mixture.

If  $\alpha_{12}=0$ , the mixture is completely random and Eq (2.35) reduces to Margules equation.

The activity coefficients can be derived from Eq (2.35) and are given by

$$\ln \gamma_1 = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + G_{12} x_1)^2} \right] \quad (2.40)$$

$$\ln \gamma_2 = x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + G_{21} x_2)^2} \right] \quad (2.41)$$

The NRTL equation does not provide any additional advantage over Margules and Van Laar equations for moderately non-ideal solutions, but it represents the excess Gibbs free energy of strong non-ideal and partially miscible systems quite satisfactorily.

### 2.2.5 UNiversal QUasi Chemical (UNIQUAC) Equation

To express the excess Gibbs free energy of a binary mixture, Abrams and Prausnitz (1975) developed the UNiversal QUasi Chemical (UNIQUAC) model. The UNIQUAC equation for  $(g^E/RT)$  contains two parts - a combinatorial part and a residual part. The combinatorial part takes into account the composition, size and shape of the constituent molecules and contains pure component properties only. The residual part takes into account the intermolecular forces and contains two adjustable parameters. The UNIQUAC equation is given by

$$\frac{g^E}{RT} = \frac{g^E}{RT}(\text{combinatorial}) + \frac{g^E}{RT}(\text{residual}) \quad (2.42)$$

where

$$\frac{g^E}{RT}(\text{combinatorial}) = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \frac{z}{2} \left( q_1 x_1 \ln \frac{\theta_1}{\phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2} \right) \quad (2.43)$$

$$\frac{g^E}{RT}(\text{residual}) = -q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{12}) \quad (2.44)$$

$$\phi_i = \text{segment fraction of component } i = \left( x_i r_i / \sum_i x_i r_i \right) \quad (2.45)$$

$$\theta_i = \text{area fraction of component } i = \left( x_i q_i / \sum_i x_i q_i \right) \quad (2.46)$$

$r_i$  = volume parameter of component  $i$

$q_i$  = surface area parameter of component  $i$

$$\tau_{ij} = \exp \left\{ - \frac{(u_{ij} - u_{ii})}{RT} \right\} = \exp \left( - \frac{a_{ij}}{T} \right) = \text{adjustable parameter} \quad (2.47)$$

$u_{ij}$  = average interaction energy for the interaction of molecules of component  $i$  with the molecules of component  $j$ ; and

$z$  = coordination number which is usually taken as 10.

From Eqs. 2.42-2.47 one can obtain the activity coefficients as

$$\ln \gamma_i = \ln \gamma_i^c (\text{combinatorial}) + \ln \gamma_i^R (\text{residual}) \quad (2.48)$$

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (2.49)$$

$$\ln \gamma_i^R = q_i \left[ 1 - \ln \left( \sum_j \theta_j \tau_{ij} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\left( \sum_k \theta_k \tau_{kj} \right)} \right] \quad (2.50)$$

where 
$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (2.51)$$

The structural parameters  $r_i$  and  $q_i$  are calculated as the sum of product of the group volume and parameters  $R_k$  and  $Q_k$ .

$$r_i = \sum_k v_k^{(i)} R_k \quad (2.52)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (2.53)$$

where  $v_k^{(i)}$  is the number of groups of type  $k$  in a molecule of component  $i$ . The UNIQUAC equation is applicable to a wide variety of liquid solutions commonly encountered by chemical engineers.

### ***2.2.7 Advantages and Disadvantages of Activity Coefficient Approach***

A simplifying assumption that is made in the development of activity coefficient models is that  $g^E$  is independent of pressure. In view of this assumption, the activity coefficient approach can be applied to systems at low to moderate pressures, far removed from the critical. For processes that operate near or above the critical, the activity coefficient approach cannot be used, which is by far the greatest deficiency of this approach.

The activity coefficient approach should be used to treat low pressure VLE data. The activity coefficient approach can be successfully applied to various types of systems: mixtures of alcohols with hydrocarbons, non-polar hydrocarbon mixtures and mixtures of alcohols with other polar compounds. In addition, systems with limited miscibility have been successfully treated with activity coefficient approach.

## ***2.3 Equation of State Approach***

In the equation of state method, a single equation of state is used to represent all fluid phases. From the thermodynamic point of view, this is a potentially more powerful approach as it provides a uniform representation of the thermodynamic properties in the two-phase and one-phase regions with a single equation. It is not only applicable to wide pressure and temperature ranges including critical and supercritical conditions but also makes it possible to calculate phase equilibria data. According to the review by Kolasinska (1986), depending on the form of equation of state variables, the equation of state may be classified into the following types.

1. Non analytical

2. Analytical

- a) inspired on a Virial expansion

- b) inspired on the two-term van der Waals form

Equations of state inspired on the two-term van der Waals form were found to be most attractive due to their simplicity, low computational costs and reliability. Non-analytical types of equations are not presented here. A brief account of the analytical type of EOS is presented below. The simplest EOS is the ideal gas equation ( $PV = nRT$ ) which considers that there are no interactions between molecules.

### 2.3.1 Virial EOS

In real gases molecular interactions always exist. This is explained by the Virial EOS where  $PV$  is expressed as a power series in  $P$  (Smith et al. 1996).

$$PV = a + bP + cP^2 + \dots \quad (2.54)$$

$$PV = a(1 + B'P + C'P^2 + \dots) \quad (2.55)$$

Where,  $a, B', C'$  are constants at a given temperature for a given species. When  $a = RT$ , Eq. (2.54) reduces to

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + \dots \quad (2.56)$$

or alternatively

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad (2.57)$$

Where, Eq. (2.56) or (2.57) is called Virial equation of state,  $Z$  is the compressibility factor and  $B, C, D$  etc., (or  $B', C', D'$  etc.,) are called virial coefficients. The virial EOS is not used in phase-equilibrium studies as it can describe only vapor phase behavior.

### Equations inspired on the two term van der Waals form

In general equations based on the van der Waals model are in a form where total pressure is the sum of an attractive and a repulsive pressure term (Kolasinska 1986).

$$P = P_{(repulsive)} - P_{(attractive)} \quad (2.58)$$

This form is proposed to take into account the attractive and repulsive forces existing in the real fluids. Imagine two molecules as hard spheres. When the molecules are at a large distance from each other they experience small or no attractive forces. As the

distance between the molecules is decreased, the attractive forces get larger, until the hard spheres come close to each other. Once the molecules come close to each other, repulsive forces start dominating until the molecules can get close no further. This volume is unavailable for the molecular motion. Van der Waals took the unavailable volume into account by introducing a parameter  $b$  called the 'excluded volume'.

### 2.3.2 van der Waals Equation of State (vdW)

When expressed in the form of Eq. (2.58) the van der Waals equation is given by,

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (2.59)$$

$$P_{\text{repulsive}} = \frac{RT}{v-b} \quad (2.60)$$

$$P_{\text{attractive}} = -\frac{a}{v^2} \quad (2.61)$$

The values of  $a$  and  $b$  can be found by regressing vapor pressure data and choosing  $a$  and  $b$  that best fit that data or alternatively critical point conditions are used. At the critical point, the first and second derivatives of pressure with respect to volume at constant temperature are zero. When these conditions are applied to Eq. (2.59), the values of  $a$  and  $b$  turn out to be

$$a = \frac{27R^2T_c^2}{64P_c} \quad (2.62)$$

$$b = \frac{RT_c}{8P_c} \quad (2.63)$$

### 2.3.3 Redlich-Kwong Equation of State

An important modification of the van der Waals equation of state was made by Redlich and Kowng (1949), who introduced a temperature dependence and slightly different volume dependence in the attractive term. The Redlich-Kwong Equation of State (RK EOS) is given by



$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)} \quad (2.64)$$

where

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c} \quad (2.65)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (2.66)$$

These modifications improved the accuracy of the equation. As before, the values of  $a$  and  $b$  can be found by fitting vapor pressure data or by using the conditions at the critical point. The RK EOS has limited accuracy, and is generally successful only for nearly ideal systems. To overcome these deficiencies, many modifications have been proposed over the years. Two of these modifications have achieved wide acceptance – the Soave and the Peng-Robinson equations of state.

### 2.3.4 Soave-Redlich-Kwong Equation of State

Soave (1972) proposed a modification to the RK Equation incorporating the temperature dependency to the EOS parameter  $a$  as

$$a(T) = a_c \alpha(T) \quad (2.67)$$

where

$$\alpha(T) = \left\{ 1 + S(1 - \sqrt{T_r}) \right\}^2 \quad (2.68)$$

$$S = 0.48 + 1.574\omega - 0.176\omega^2$$

Thus, the EOS proposed by Soave is of the form

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (2.69)$$

In Equation (2.67)  $a_c$  can be expressed as

$$a_c = 0.42748 \frac{R^2 T_c^2}{P_c} \quad (2.70)$$

$$b_c = 0.08664 \frac{RT_c}{P_c} \quad (2.71)$$

When calculating fugacity coefficients, it is convenient to write the equation in terms of the compressibility factor  $Z$ . In this form the Soave equation of state is

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (2.72)$$

where

$$A = \frac{aP}{R^2T^2} \quad (2.73)$$

$$B = \frac{bP}{RT} \quad (2.74)$$

$$Z = \frac{Pv}{RT} \quad (2.75)$$

The van der Waals one fluid mixing rules are used for calculating  $a$  and  $b$  of the mixture. Thus the fugacity coefficient of component  $i$  in a mixture is given by

$$\ln \phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) + \frac{a}{bRT} \left[ \frac{b_i}{b} - 2\sqrt{\frac{a_i}{a}} \right] \ln \left[ \frac{Z+B}{Z} \right] \quad (2.75)$$

### ***2.3.5 Advantages and Disadvantages of Equation of state approach***

In the Equation of State approach the definition of fugacity coefficient is used to describe both liquid and vapor phases through the application of single equation of state. The major advantage of this approach is its applicability over a wide range of pressures including critical and supercritical pressures. However, phase equilibrium calculations by these methods are rather lengthy except for a simple equation of state. Another problem associated with the use of the EOS technique is the insufficiency of information about the exact form of the EOS for mixtures, and the inaccuracy of the existing mixing rules for mixtures containing polar and hydrogen bonding components.

## **CHAPTER 3**

# **LITERATURE REVIEW**

The synthesis and design of separation processes requires a reliable knowledge of the phase behavior of the system to be separated. For the description of multicomponent non-electrolyte systems,  $g^E$ -models or equations of state can be applied using binary data alone. Experimental data are however often missing. In such cases group contribution methods such as ASOG (Derr and Deal, 1969; Kojima and Tochigi, 1979), UNIFAC (Fredenslund et al., 1975, 1977) and modified UNIFAC (Dortmund) (Weidlich and Gmehling, 1987; Gmehling et al., 1993; Lohmann et al., 1998; Larsen et al., 1987) can be successfully applied. These methods are developed for the prediction of vapor-liquid equilibria (VLE), so that the required group interaction parameters were mainly fitted to experimental VLE data stored in the Dortmund Data Bank (Gmehling, 1985, 1991). The actual parameters of these methods were published by Hansen et al. (1991) and Tochigi et al. (1990).

Koji Arita et al. (1991) measured the isothermal vapor-liquid Equilibria (VLE) data for the systems chlorofluoromethane (HCFC-22) and 1,1,1,2-tetrafluoroethane (HFC-134a) over the temperature range 273.16 to 323.16 K. The data obtained were correlated with use of the Redlich-Kwong-Soave (Soave, 1972) equation of state with one interaction parameter. The critical constants of HCFC22 and HFC134a were taken from the literatures (Japanese Association of Refrigeration, 1975; Wilson and basu, 1988). The acentric factors used in this study, which were calculated by using the generalized Frost-Kalkwarf-Thodos vapor-pressure correlation (Reid et al., 1977), were 0.2222 for HCFC22 and .3259 for HFC134a, respectively.

Hironobu Kubota et al. (1990) measured the isothermal VLE data for the system chlorodifluoromethane (HCFC22) + 1-chloro-1, 1-difluoroethane (HCFC142b) over the temperature range 263 to 338 K and pressure 0.1 to 2.7 MPa. Data at 263.15 and 293.15 K measured by Nagahama et al. show maximum deviation of 2.2 and 3.3 mole percent with present experimental data respectively. To correlate the present phase equilibrium data, the Peng-Robinson equation (PR) of state with suitable binary interaction parameter  $k_{ij}$  used.

VLE data for seven binary fluorocarbon mixtures were modeled using the Wong-Sandler (WS) model (1998). A variety of fluorocarbon azeotropes were chosen for testing the accuracy of the model. The azeotropes tested were  $\text{CF}_2\text{H}_2$  and  $\text{CF}_3\text{CH}_3$ ,  $\text{CF}_2\text{H}_2$  and  $\text{CF}_3\text{CF}_3$ ,  $\text{CF}_2\text{H}_2$  and  $\text{CHF}_2\text{CF}_3$ ,  $\text{CF}_2\text{H}_2$  and  $\text{CH}_3\text{CH}_2\text{CH}_3$ ,  $\text{CF}_3\text{H}$  and  $\text{CF}_3\text{CF}_3$ ,  $\text{CF}_3\text{CF}_3$  and  $\text{CO}_2$ ,  $\text{CHF}_2\text{CF}_3$  and  $\text{NH}_3$ . Using the WS mixing rule and non-random two liquid (NRTL) activity coefficient model, a three parameter fit was calculated for each binary mixture. The single adjustable parameter ( $k_{ij}$ ) for each binary pair is referred to as the WS mixing rule parameter ( $k_{12}$ ). Four excess free energy (or equivalently activity coefficient) models were evaluated for calculating  $G^{\text{ex}}$ : UNIQUAC, Van Laar, Wilson, and NRTL. In all cases the NRTL model with WS mixing rule provided the best fit with VLE data.

Yun Whan Kang et al. (1996) measured the isothermal VLE data for the three binary systems HFC-32 + HCFC-22, HFC-32 + CFC-12, and HFC-32 + HCC-40 at  $10^\circ\text{C}$  and correlated with the Wilson equation. The difluoromethane (HFC-32) + dichlorodifluoromethane (CFC-12) system forms a minimum boiling azeotrope, but the other do not.

Min Young Jung et al. (2001) measured the isothermal VLE data of the binary system difluoromethane (HFC-32) + pentafluoroethane (HFC-125) over the temperature range from 268.15 K to 308.15 K and correlated with the Carnahan-Starling-De Santis (CSD), Peng-Robinson (PR), and Redlich-Kwong-soave (RKS) equations of state. Higashi and Kobayashi and Nishiumi have published experimental data for the VLE for HFC-32 + HFC-125. The binary interaction parameter for the CSD equation of state has stronger temperature dependence than those for the RKS and PR equations of state. The average deviation between the measured pressure and calculated results from the CSD equation of state is about 0.18% and that from the PR equation state is about 0.22%. The average deviation from RKS equation of state is about 0.58%. As a result, the CSD equation of state correlates the experimental data better than the PR and RKS equations of state.

Eui-Yeop Chung et al. (1997) measured the isothermal VLE data of the binary mixture of HFC-32/134a over the temperature range from 263 K to 323 K and correlated with the Peng-Robinson and Redilch-Kwong-Soave equations of state. The relative pressure deviation for two cases was generally less than 0.2% for the temperature range investigated, and the difference is not significant considering the uncertainty of pressure

investigated, and the difference is not significant considering the uncertainty of pressure measurements. Measured deviation of pressure and composition using Peng-Robinson equation of state correlates experimental data better than the Redlich-Kwong-Soave (RKS) equation of state.

Chang Nyeon Kim et al. (2000) measured the isothermal VLE data of the binary system of difluoromethane (HFC-32) + 1,1,1-trifluoroethane (HFC-143a) over the temperature range from 263.15 K to 313.15 K and correlated with The Canahan-Starling-DE Santis (CSD), Peng-Robinson (PR), and Redilch-Kwong-Soave (RKS) equations of state using van der Waals mixing rules. It is evident that the binary interaction parameter for the CSD equation of state increases slightly as the temperature increases. On the other hand, the binary interaction parameters for both the PR and RKS equations of state decrease as the temperature increases. The binary interaction parameter for the RKS equation of state has larger temperature dependence than those for the CSD and PR equations of state. The average deviation between the measured pressure and the calculated results from the CSD equation of state is about 0.29% and that from the PR equation of state is about 0.45%. The average deviation from the RKS equation of state is about 0.70%. As result, the CSD equation of state correlates the experimental data better than the PR and RKS equation of state.

Jaewon Lee et al. (1996) measured the P, T, x, y data for HFC-134a + HCFC-124 and HCFC-124 + HCFC-142b and correlated the results with the Peng-Robinson equation of state using the van der Walls one fluid mixing rule. Neither HFC-134a + HCFC-124 nor HCFC-124 + HCFC-142b shows azeotropic behavior at the temperature studied.

Sergio Bobbo et al. (1998) measured the VLE data for the systems 1,1,1,2-tetrafluoroethane + isobutene (R134a + R600a) at 293.66 and 303.68 K, 1,1,1,2-tetrafluoroethane + 1,1,1,3,3,3-hexafluoropropane (R134a + R236fa) at 283.62 and 303.68 K and isobutene + 1,1,1,3,3,3-haxafluoropropane (R600a + R236fa) and correlated with Redlich-Kwong-Soave equation of state with the Huron-Vidal mixing rules was used the relevant Margules equation. The R134a + R236fa system was almost ideal. On other hand both of the binaries R134a + R600a and R600a + R236fa composed of a hydrocarbon (here R600a) and the relatively highly fluorinated R134a or R236fa.

exhibited positive homogeneous azeotropes with qualitatively similar deviations from *Raoult's* law.

C.N Kim et al. (1999) measured the isothermal VLE data of the system HFC-143a + HFC-134a over the temperature range from 263.15 to 313.15 K at 10 K intervals and correlated with the Carnahan-Starling-De Santis (CSD) and Peng-Robinson (PR) equation of state. The Binary interaction parameters for both the PR and the CSD equations of state decrease as the temperature increases. The present data were in good agreement with the calculated results from the CSD equations of state, and the deviations were less than 1.0% with the exception of two points.

Michael Kleiber (1995) measured the VLE data for the systems R134a-R23, R134a-R114, R13B1-R23, R134a-dimethylether, R13B1-R13 and R142b-dimethyl ether over the temperature range 251 to 298 K, and pressure up to 2MPa and correlated with UNIFAC equation. The consistency of the data has been shown by a maximum likelihood method. This paper also published optimized UNIFAC group assignment for refrigerants.

Michael Kleiber (1994) and coworkers obtained the VLE for the binary mixtures propylene-R12, propylene-R22, propylene-R152a, propylene-R13, propylene-R23, propylene-R134a, propylene-R115, propylene-R13B1, propylene-R114, propylene-R116, R134a-R12, R134a-R152a, R134a-R116, R134a-R12, R134a-propane at temperatures between 251 and 298 K and pressure up to 2 MPa. He showed the consistency of the data by a maximum-likelihood method. He also correlated the data by generalized forms of various EOS such as Peng-Robinson, Peng-Robinson-Stryjeck-vera, Redlich-kwong-soave and Lee-Kesler-Plocker along with appropriate mixing rules. These EOS were fitted to the experimental data by optimizing the binary interaction parameters. Considering the fitting rules, The LKP equation seems to perform worse than the others, especially for azeotropic mixtures like propylene-R152a, propylene-R115, propylene-R134a, R134a-propane R134a-R12. The PR, RKS and PRSV equations yield similar results in each case. The system R134a-R116 was described significantly worse than the other mixtures. Only the PRSV equation with the Vanlaar type was able to describe it satisfactorily. This mixing rule is, of course, superior to the others, because it has two adjustable parameters instead of only one, but usually it gives only slightly better results than normal vdW mixing rule

## CHAPTER 4

# PREDICTION OF VLE DATA

The purpose of phase-equilibrium thermodynamics is to predict the conditions ( $T$ ,  $P$ , composition) prevailing when two or more phases are in equilibrium. The thermodynamic equations which determine the state of equilibrium between vapor and liquid phases are  $T^l = T^v$  ( $T$  is constant),  $P^l = P^v$  ( $P$  is constant), and  $f_i^l = f_i^v$ . To find the conditions which satisfy these equations, it is necessary to have a method for evaluating the fugacity ( $f_i$ ) of each component in both vapor and liquid phases. This can be done using the basic thermodynamic equation for calculating the fugacity coefficient ( $\phi_i^l$  or  $\phi_i^v$ ).

The fugacity coefficient can be obtained by using the relation

$$\ln \left( \frac{f_i}{y_i P} \right) = \ln \phi_i = \frac{1}{RT} \int_0^P \left( \bar{v}_i - \frac{RT}{P} \right) dP \quad (4.1)$$

Where  $\bar{v}_i = \left( \frac{\partial V}{\partial n_i} \right)_{T,P,n} =$  the partial molar volume.

Or,

$$\ln \left( \frac{f_i}{y_i P} \right) = \ln \phi_i = \frac{1}{RT} \int_v^\infty \left( \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n} - \frac{RT}{V} \right) dV - \ln Z \quad (4.2)$$

The solution to the phase-equilibrium problem is provided completely by either one of these equations together with an EOS and the equations of phase-equilibrium. Eq. (4.1) is used when the EOS is given in volume explicit form ( $V = V_i(P, T, n_1, n_2, \dots)$ ) whereas Eq. (4.2) is used when the EOS is in the pressure explicit form ( $P = P_i(V, T, n_1, n_2, \dots)$ ). Most of the EOS are pressure explicit type. To use an EOS, one must transform the EOS in molar form to a total form first. When one is to calculate the fugacity of component  $i$  in the mixture at a specified  $T$ ,  $P$ , and composition, differentiate the EOS w.r.t  $n_i$ , and substitute in Eq. (4.2) to get the result.

There are basically four classes of VLE problems:

*BUBLP*: Calculate  $\{y_i\}$  and  $P$ , given  $\{x_i\}$ ,  $T$ .

*DEWP*: Calculate  $\{x_i\}$  and  $P$ , given  $\{y_i\}$ ,  $T$ .

*BUBLT*: Calculate  $\{y_i\}$  and  $T$ , given  $\{x_i\}$ ,  $P$ .

*DEWT*: Calculate  $\{x_i\}$  and  $T$ , given  $\{y_i\}$ ,  $P$ .

The problems of engineering interest generally deal with *BUBLP* or *DEWP*. In order to correlate the experimental data, choice of the model to calculate the fugacity coefficients and the determination of the best or the most representative parameters for the model are the most important steps. The models in this chapter are based on the PR EOS and Quartic EOS, each combined separately with *vdW* mixing rules and composition dependent two parameter mixing rules.

#### ***4.1 UNIQuac Functional group Activity Coefficients (UNIFAC) Method (group contribution method)***

To correlate and to predict the thermodynamic properties of a solution it was convenient to consider the component molecules as a collection of functional groups. The functional groups are structural units such as  $-\text{CH}_3$ ,  $-\text{OH}$  and others which when added form the constituent molecules. In the group contribution methods, a solution of components is treated as a solution of groups. The activity coefficients of the components are then determined by the properties of the functional groups rather than by those of the molecules. The basic idea behind this approach is that there are several thousands of chemical compounds that are of interest to a chemical engineer but the number of functional groups, which constitute these compounds, is very small. The activity coefficients in a large number of solutions can be calculated from the parameters characteristic of the functional groups.



In the UNIFAC method the activity coefficients consist of two parts, a combinatorial part ( $\ln \gamma_i^C$ ) and a residual part ( $\ln \gamma_i^R$ ). To evaluate  $\ln \gamma_i^C$  only pure component data is required.

$$\ln \gamma_i = \ln \gamma_i^C (\text{combinatorial}) + \ln \gamma_i^R (\text{residual}) \quad (4.3)$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (4.3)$$

where 
$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (4.4)$$

The structural parameters  $r_i$  and  $q_i$  are calculated as the sum of product of the group volume and parameters  $R_k$  and  $Q_k$ .

$$r_i = \sum_k v_k^{(i)} R_k$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (4.5)$$

where  $v_k^{(i)}$  is the number of groups of type  $k$  in a molecule of component  $i$ .

The residual part of the activity coefficient  $\ln \gamma_i^R$  is given by

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left( \ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (4.6)$$

(all groups)

where

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right] \quad (4.7)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} = \text{surface area fraction of group } m \quad (4.8)$$

$$\psi_{mn} = \exp \left( - \frac{u_{mn} - u_{nn}}{RT} \right) = \exp \left( - \frac{a_{mn}}{T} \right) \quad (4.9)$$

$x_m$  = mole fraction of group  $m$  in the mixture

$a_{mn}$  = group interaction parameter (in K).  $a_{mn} \neq a_{nm}$

$u_{mn}$  = measure of interaction energy between groups  $m$  and  $n$

$\Gamma_k$  = group residual activity coefficient; and

$\Gamma_k^{(i)}$  = residual activity coefficient of group  $k$  in a reference solution containing only molecules of type  $i$ .

## 4.2 Modified UNIQuac Functional group Activity Coefficients (Modified UNIFAC) Method (group contribution method)

In the Modified UNIFAC method the activity coefficients consist of two parts, a combinatorial part ( $\ln \gamma_i^c$ ) and a residual part ( $\ln \gamma_i^R$ ). To evaluate  $\ln \gamma_i^c$  only pure component data is required.

$$\ln \gamma_i = \ln \gamma_i^c (\text{combinatorial}) + \ln \gamma_i^R (\text{residual}) \quad (4.10)$$

The combinatorial part of the activity coefficient  $\ln \gamma_i^c$  is given by

$$\ln \gamma_i^c = 1 - V_i^* + \ln V_i^* - 5q_i \left( 1 - \frac{V_i^*}{F_i} + \ln \left( \frac{V_i^*}{F_i} \right) \right) \quad (4.11)$$

The parameter  $V_i^*$  can be calculated by using the relative van der Waals volumes  $R_k$  of the different groups.

$$V_i^* = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \quad (4.12)$$

$$V_i = \frac{r_i}{\sum_j x_j r_j} \quad (4.13)$$

$$r_i = \sum_k v_k^{(i)} R_k \quad (4.14)$$

$$F_i = \frac{q_i}{\sum_j x_j q_j} \quad (4.15)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (4.16)$$

where  $v_k^{(i)}$  is the number of groups of type  $k$  in a molecule of component  $i$ .

The residual part of the activity coefficient  $\ln \gamma_i^R$  is given by

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left( \ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (4.17)$$

(all groups)

where

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right] \quad (4.18)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (4.19)$$

$$X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_n v_n^{(i)} x_i} \quad (4.19)$$

$$\psi_{mn} = \exp \left( \frac{a_{mn} - b_{mn} T - c_{mn} T^2}{T} \right) \quad (4.20)$$

$x_m$  = mole fraction of group  $m$  in the mixture

$a_{mn}$  = group interaction parameter (in K).  $a_{mn} \neq a_{nm}$

$b_{mn}$  = group interaction parameter (in K).  $b_{mn} \neq b_{nm}$

$c_{mn}$  = group interaction parameter (in K).  $c_{mn} \neq c_{nm}$

$u_{mn}$  = measure of interaction energy between groups  $m$  and  $n$

$\Gamma_k$  = group residual activity coefficient: and

$\Gamma_k^{(i)}$  = residual activity coefficient of group  $k$  in a reference solution containing only molecules of type  $i$ .

### 4.3 Peng-Robinson Equation with van der Waals one fluid mixing rules

#### 4.3.1 Peng-Robinson Equation of State

In 1976, Peng and Robinson introduced another equation of state, which extended some of the ideas presented by Soave. The repulsive part of the van der Waals model remained the same, but just as Soave had done, the temperature dependence of the attractive term was incorporated into the  $a$  term. The denominator of the attractive term was also changed to a slightly more complicated expression of volume and the size parameter. The Peng-Robinson Equation of State is given by

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (4.21)$$

$$\text{where } b = 0.07780 \frac{RT_c}{P_c} \quad (4.22)$$

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (4.23)$$

$$a(T) = a(T_c) \alpha \quad (4.24)$$

$$\alpha^{\frac{1}{2}} = 1 + S(1 - T_r^{\frac{1}{2}}) \quad (4.25)$$

where reduced temperature

$$T_r = T / T_c \quad (4.26)$$

$$S = f(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (4.27)$$

and  $\omega$  is the Pitzer (1995) acentric factor defined as

$$\omega = -\log_{10} P_r^s|_{T_r=0.7} - 1.0 \quad (4.28)$$

where

$$P_r^s = P^s / P_c = \text{reduced pressure at } T_r = 0.7 \quad (4.29)$$

### 4.3.2 van der Waals one fluid Mixing Rules

These are also called the classical mixing rules and are given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (4.30)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (4.31)$$

Where  $a$  is the energy parameter and  $b$  is the volume parameter.  $a_{ij}$  and  $b_{ij}$  are the cross terms i.e. the interaction terms when ( $i \neq j$ ) whereas  $i$  and  $j$  represent the components( $c$ ).

$$a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \quad (4.32)$$

$$b_{ij} = \left( \frac{b_{ii} + b_{jj}}{2} \right) (1 - l_{ij}) \quad (4.33)$$

Where  $k_{ij}$  and  $l_{ij}$  are the binary interaction parameters:  $l_{ij}$  being zero most of the times. When Eq. (4.34) is applied to Eq. (4.33) with  $l_{ij} = 0$ , it reduces to a linear term.

$$b = \sum_i x_i b_{ii} \quad (4.34)$$

The above vdW one fluid mixing rules are used for van der Waals, Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson equations of state with a single binary interaction parameter  $k_{ij}$ . ( $l_{ij} = 0$ ).

The PR EOS expressed on a total basis, in pressure explicit form, is

$$P = \frac{n_t RT}{V - n_t b} - \frac{n_t^2 a(T, \omega)}{V(V + n_t b) + n_t b(V - n_t b)} \quad (4.35)$$

where  $V = v n_t$  and  $n_t$  = total number of moles

Eq. (4.35) when differentiated on molar basis and substituted in Eq. (4.2) with the use of van der Waals one fluid mixing rules (Eqs. (4.30) through (4.34)) gives the following expression for the fugacity coefficient.

$$\ln \hat{\phi}_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{a}{2\sqrt{2}bRT} \left[ \frac{b_i}{b} - 2\sqrt{\frac{a_i}{a}} \right] \ln \left[ \frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})} \right] \quad (4.36)$$

$$\text{where} \quad B = \frac{bp}{RT} \quad (4.37)$$

Eq. (4.36) is used to calculate the fugacity coefficient of either liquid or vapor phase, by using the appropriate compressibility factor and the composition.

#### 4.4 VLE Calculations

The most important step of calculating the fugacity coefficients ( $\phi_i^l$  or  $\phi_i^v$ ) is carried out by using the Peng-Robinson equation. This requires  $Z^l$ , the liquid phase compressibility factor or  $Z^v$ , the vapor phase compressibility factor. These are obtained by solving the EOS which is expressed in terms of the compressibility factor  $Z$ .

For PR EOS, we can obtain the  $Z^l$  and  $Z^v$  by solving the following cubic EOS which is expressed in terms of the compressibility factor  $Z$ .

$$Z^3 + (B - 1)Z^2 + (A - 3B^2 - 2B)Z + (B^2 + B^3 - AB) = 0 \quad (4.38)$$

where

$$A = \frac{aP}{R^2T^2} \quad (4.39)$$

$$B = \frac{bP}{RT} \quad (4.40)$$

$$Z = \frac{PV}{nRT} \quad (4.41)$$

#### 4.4.1 Newton –Raphson Method.

In general Neton –Raphson method expressed is

$$x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)} \quad (4.42)$$

Above Eq. (4.38) expressed interms Newton Raphson method.

$$f(Z) = Z^3 + (B-1)Z^2 + (A-3B^2-2B)Z + (B^2 + B^3 - AB) \quad (4.43)$$

$$Z_{i+1} = Z_i - \frac{f(Z_i)}{f'(Z_i)} \quad (4.44)$$

above Eq. (4.44) solving to obtain one root of  $Z'_1$  or  $Z''_1$ . To find the other two roots using Quadratic equation.

#### 4.4.2. Solution of Quadratic Equation.

In general form of the Quadratic equation is

$$ax^2 + bx + c = 0 \quad (4.45)$$

$$\text{discriminant} = b^2 - 4ac \quad (4.46)$$

if disriminant is less than zero roots are imaginary. discriminant is equal zero roots are equal and discriminant greater than zero roots are real. Two roots are expressed is

$$\text{root1} = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad (4.47)$$

$$\text{root2} = \frac{-b - \sqrt{b^2 - 4ac}}{2a} \quad (4.48)$$

Compressibility factor expressed in terms of Quadratic equation.

$$Z^2 + (Z'_1 - (1-B))Z + (Z'^2_1 - Z'_1(1-B) + (A-3B^2-2B)) = 0 \quad (4.49)$$

above Eq. (4.49) write in terms of general formula

$$a=1. \quad (4.50)$$

$$b = (Z'_1 - (1-B)) \quad (4.51)$$

$$c = (Z'^2_1 - Z'_1(1-B) + (A-3B^2-2B)) \quad (4.52)$$

The values of a, b and c substituting Eq. (4.46) through (4.48) to obtain two roots of the liquid or vapor compressibility factors.

Eq. (4.38) when solved gives three roots. There are two possibilities: either all the three roots are real or only one real root (remaining two being complex). When there are three real roots, the smallest root is the liquid phase compressibility factor and the largest root is the vapor phase compressibility factor, intermediate root being meaningless. If it is only one root, it is taken either as the liquid phase or vapor phase compressibility factor depending on the calculations.

#### 4.6 Data Reduction

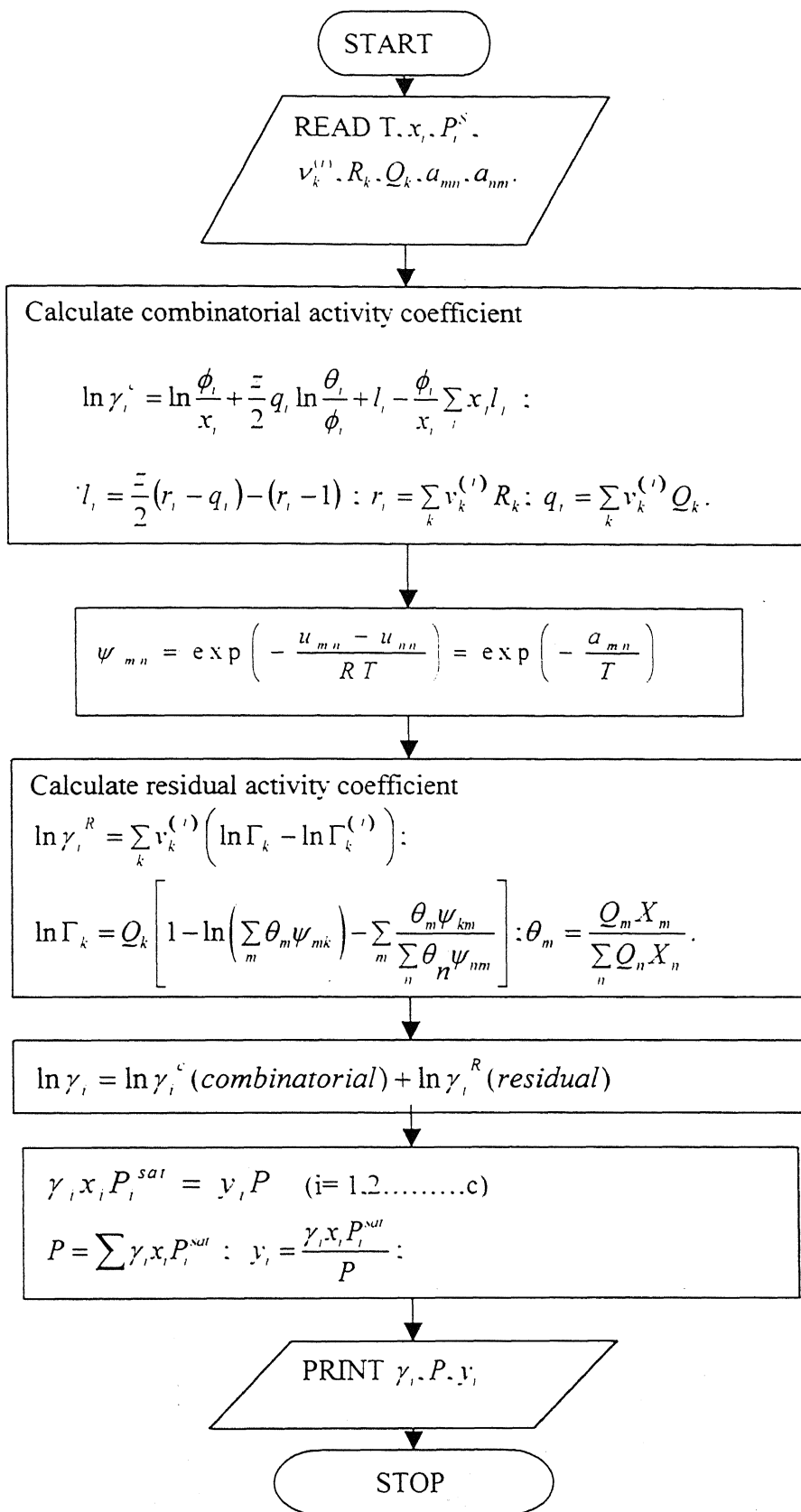
As mentioned earlier, there are two important steps i) model selection and ii) evaluation of the best parameters for the model. This needs reduction of the VLE data. In this work, only  $P$ - $x$ - $y$  data (given  $T$  and  $x_i$ ) is used. The average absolute deviations in pressure and composition are calculated from the relations.

$$\frac{\Delta P}{P} = \sqrt{\frac{1}{N} \sum_{i=1}^N \left( \frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2} \quad (4.53)$$

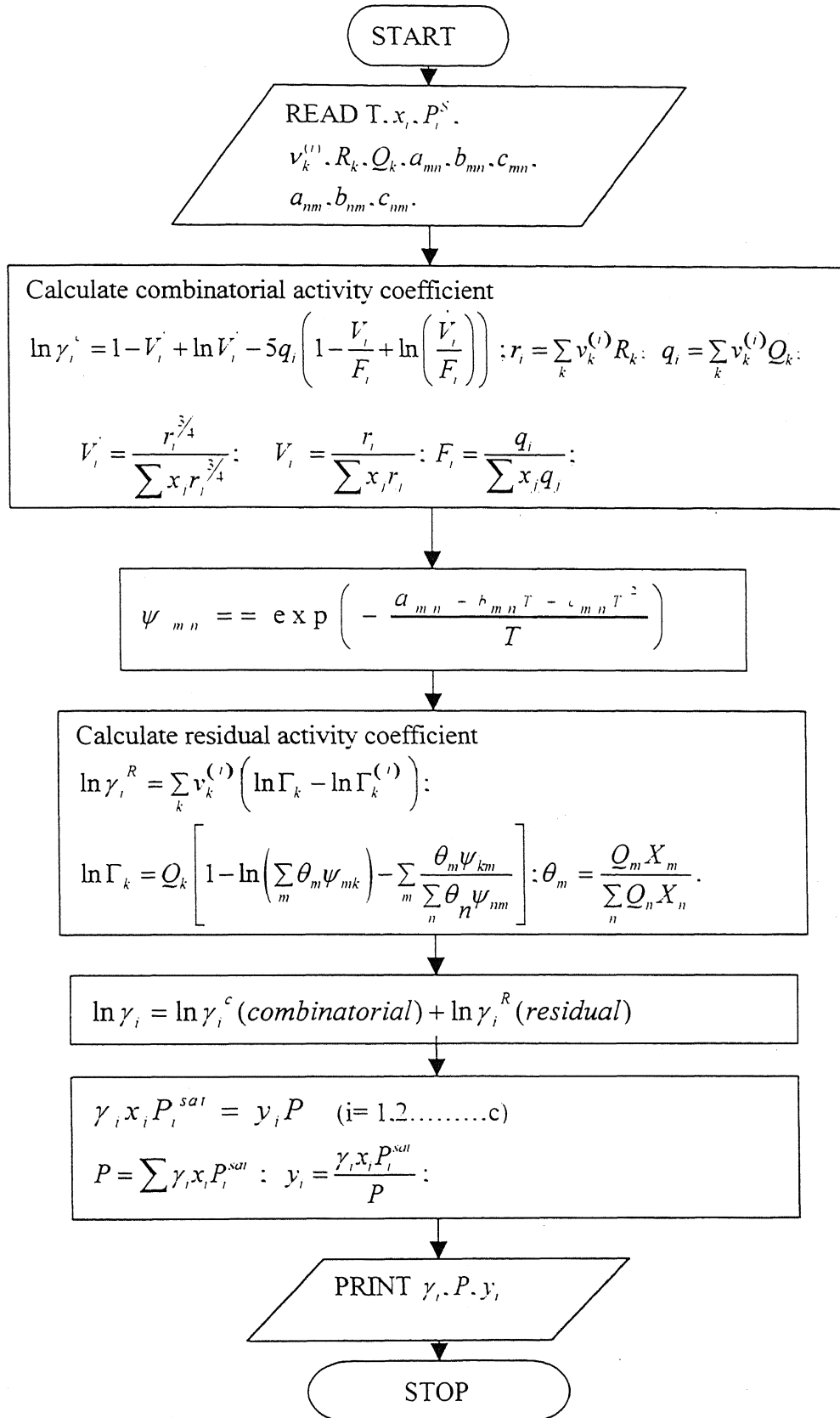
$$\overline{\Delta y} = \sqrt{\frac{1}{N} \sum_{i=1}^N (y_{1\text{exp}} - y_{1\text{cal}})^2} \quad (4.54)$$

where,  $P_{\text{exp}}$ ,  $P_{\text{cal}}$  are experimental and calculated pressure respectively.  $y_{1\text{exp}}$ ,  $y_{1\text{cal}}$  are experimental and calculated vapor phase compositions of component 1, and  $N$  is the number of data points.

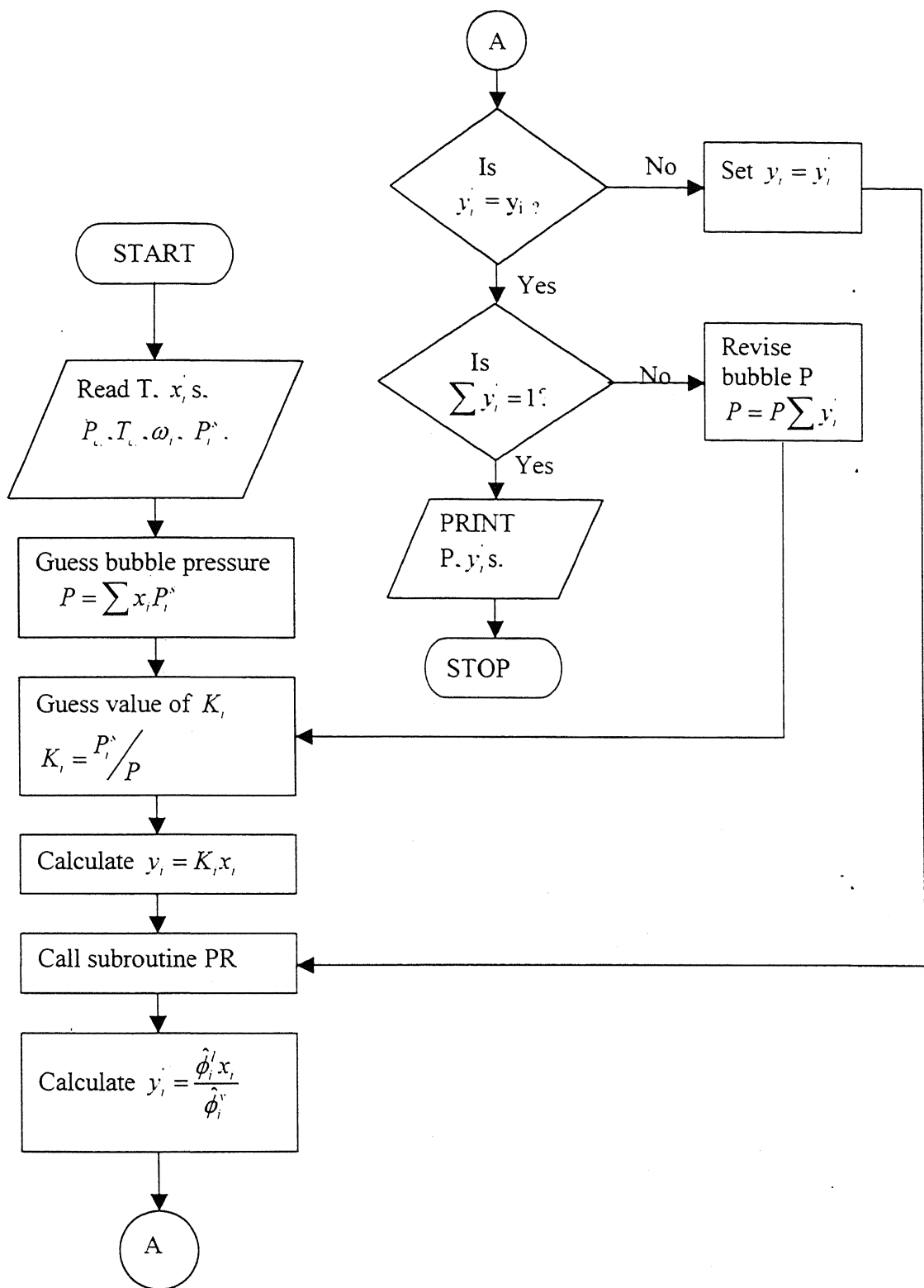




**Fig 4.1. Algorithm for VLE calculation using UNIFAC Method.**

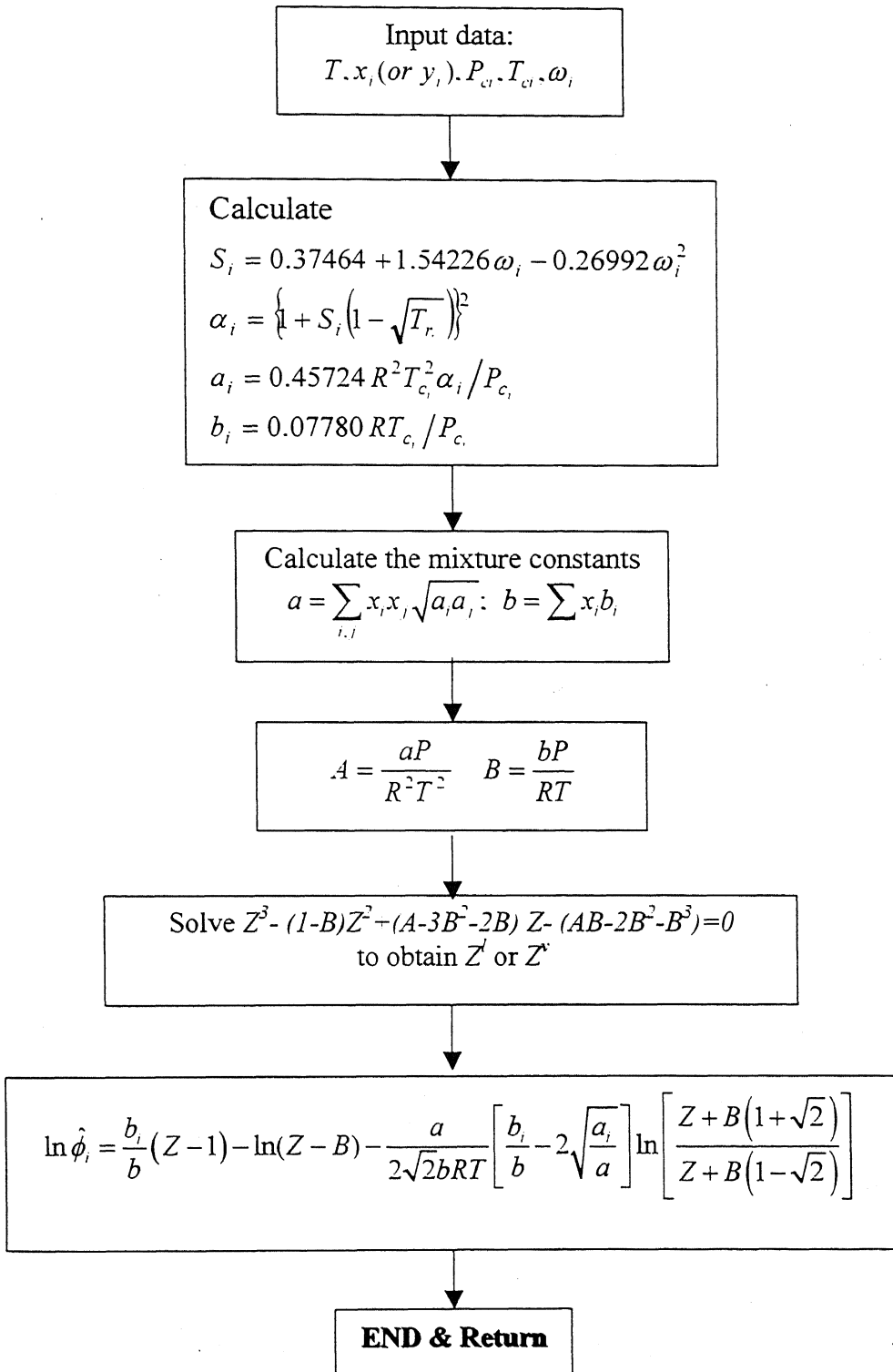


**Fig 4.2. Algorithm for VLE calculation using Modified UNIFAC Method.**



**Fig 4.3. Algorithm for bubble pressure calculation using an equation of state**

### Subroutine PR



**Fig 4.4. Subroutine for Peng-Robinson equation of state.**

## CHAPTER 5

# RESULTS AND DISCUSSION

### 5.1 Results

The results obtained from the UNIFAC, modified UNIFAC and Peng-Robinson with van der Waals one fluid one mixing rule are presented in this section. The results obtained with these three models are compared to ascertain the best model. A total of 31 binary systems at different temperatures were studied. These systems are classified into 15 different classes, such as HCFC/HFC, HCFC/HCFC, HFC/CFC, HFC/HCFC, HFC/HFC, HFC/FC, BrFC/CFC, HFC/HC, HFC/HOC, HCFC/HOC, HC/CFC, HC/HCFC, HC/HFC, HC/FC, HC/BrFC. Table (5.1) represents the source of the experimental data of all the systems and study all the systems different temperatures. The nomenclature, critical constants and acentric factors of the compounds (Reid et al. 1987) are listed in Table (5.2). Optimized UNIFAC group interaction, volume and surface area parameters of the refrigerants are listed in Table (5.3). Optimized Modified UNIFAC group interaction, volume and surface area parameters of the refrigerants are listed in Table (5.4). Only isothermal VLE (BUBLP) data is considered.

The average absolute deviations in pressure and vapor-phase composition of the all systems studied are presented in Table (5.5). The pressure ( $P$ ) and vapor-phase composition ( $y_i$ ) of one system at one temperature are presented in Tables (5.6) - (5.27). The minimum percent deviations observed for pressure and vapor-composition are 0.49 and 0.35 respectively and the corresponding maximum values are 30.80 and 14.52. Figures (5.1) – (5.11) represents the pressure ( $P$ ), liquid composition ( $x$ ), and vapor composition ( $y$ ) of the each system at particular temperature.

## 5.2 Discussion

In this work thirty-one systems of different classes at different temperatures have been studied using the UNIFAC, modified UNIFAC and PR EOS with vdW one fluid-mixing rule. The performances of the models are different for different classes of systems considered in the work.

For HCFC / HFC class of system (R22-R134a), which is non-azeotropic in nature, the P-R EOS with vdW one fluid mixing rule Predicted the VLE data better than other two models. For HCFC / HCFC class of system (R22-R142b and R124-R142b), For R22-R142b system, the VLE data obtained by the P-R with vdW one fluid mixing rule better than other two models and R124-R142b system, the VLE data obtained by the UNIFAC model better than other two models.

For HFC /CFC class of systems (R32-R12 and R143a-R12), the VLE data obtained by the UNIFAC model better than other two models. For HFC/HCFC class of systems (R32-R22, R134a-R124 and R134a-R142b), for R32-R22 system, the VLE data obtained by the UNIFAC model better than the other two models, R134a-R124 system, the VLE data obtained by the Modified UNIFAC model better than other two models and R134a-R142b system, the VLE data obtained by the P-R with vdW one fluid mixing rule better than other two models.

For HFC / HFC class of systems (R32-R125, R32-R134a, R32-R143a, R134a-R152a, R134a- R236fa and R143a-R134a), the VLE data obtained by the P-R with vdW one fluid mixing rule better than other two models. For HFC /FC class of systems (R23-R116 and R134a-R116), the VLE data obtained by UNIFAC model better than other two models. For BrFC / CFC class of system (R13B1-R13), the VLE obtained by the P-R with vdW one fluid mixing rule better results than other two models.

For HFC / HC class systems (R134a –R290 and R134 –R660a), the VLE data obtained by the Modified UNIFAC model better results than other two models. For HFC/HOC class systems (R134a-Dimethyl ether), the VLE data obtained by the Modified UNIFAC model better than other two models. . For HCFC/HOC class systems (R142b-Dimethyl ether), the VLE data obtained by the Modified UNIFAC model better than other two models.

For HC / CFC class of systems (Propylene-R12, Propylene-R13 and Propylene-R115), the VLE data obtained by the UNIFAC model better than other two models. For HC / HCFC class of systems (Propylene-R22 and Propylene-R142b), the VLE data obtained by the UNIFAC model better than other models. For HC /HFC class of systems (R600a-R236fa, Propylene-R134a and Propylene-R152a), the VLE data obtained by the UNIFAC model better than other two models. For HC / FC class of system (Propylene-R116), the VLE data obtained by the UNIFAC model better than other two models. For HC / BrFC class of system (Propylene-R13B1), the VLE data obtained by the Modified UNIFAC model better than other two models.

This study indicates that well known UNIFAC model displays better abilities in general as compared to the Modified UNIFAC model and Peng-Robinson EOS with van der Waal one fluid-mixing rule. But for HCFC/HFC, HFC / HFC class of systems P-R with vdW one fluid-mixing rule gave better results and HFC/HC, HFC/HOC, HCFC/HOC .class of systems Modified UNIFAC method gave better results.

**Table 5.1. Source of Experimental data for the systems.**

S.No	System	Data Source
1.	R22 – R134a	Koji Arita et al. (1991)
2.	R22 – R142b	Hironobu Kubota et al. (1990)
3.	R23 – R116	M.B. Shiflett et al. (1998)
4.	R32 – R12	Yun Whan Kang et al. (1996)
5.	R32 – R22	Yun Whan Kang et al. (1996)
6.	R32 – R125	Min Young Jung et al. (2001)
7.	R32 – R134a	Eui-Yeop Chung et al. (1997)
8.	R32 – R143a	Chang Nyeon Kim (2000)
9.	R13B1 – R13	Michael Kleiber (1995)
10.	R124 – R142b	Jaewon Lee et al. (1996)
11.	R134a – R12	Michael Kleiber (1994)
12.	R134a – R116	Michael Kleiber (1994)
13.	R134a – R124	Jaewon Lee et al. (1996)
14.	R134a – R142b	Michael Kleiber (1994)
15.	R134a – R152a	Michael Kleiber (1994)
16.	R134a – R236fa	Sergio Bobbo et al. (1998)
17.	R134a – R290	Michael Kleiber (1994)
18.	R134a – R600a	Sergio Bobbo et al. (1998)
19.	R134a – Dimethyl ether	Michael Kleiber (1995)
20.	R142b – Dimethyl ether	Michael Kleiber (1995)
21.	R143a – R134a	C.N. Kim et al. (2000)
22.	R600a – R236fa	Sergio Bobbo et al. (1998)
23.	Propylene – R12	Michael Kleiber (1994)
24.	Propylene – R13	Michael Kleiber (1994)



(Continued)

25.	Propylene – R22	Michael Kleiber (1994)
26.	Propylene – R13B1	Michael Kleiber (1994)
27.	Propylene – R115	Michael Kleiber (1994)
28.	Propylene – R116	Michael Kleiber (1994)
29.	Propylene – R134a	Michael Kleiber (1994)
30.	Propylene – R142b	Michael Kleiber (1994)
31.	Propylene – R152a	Michael Kleiber (1994)

**Table 5.2. Nomenclature, Critical properties and acentric factors of the refrigerants.**

S.No	Refrigerant	Formula	Chemical name	T <sub>c</sub> (K)	P <sub>c</sub> (bar)	ω
1.	R12	C <sub>2</sub> Cl <sub>2</sub> F <sub>2</sub>	Dichlorodifluoromethane	385.00	41.40	0.2040
2.	R13	C <sub>2</sub> ClF <sub>3</sub>	Chlorotrifluoromethane	302.00	38.70	0.1980
3.	R22	CH <sub>2</sub> ClF <sub>2</sub>	Chlorodifluoromethane	369.30	49.70	0.2210
4.	R23	CHF <sub>3</sub>	Trifluoromethane	299.30	48.60	0.2600
5.	R32	CH <sub>2</sub> F <sub>2</sub>	Difluoromethane	351.60	58.30	0.2710
6.	R13B1	C <sub>2</sub> F <sub>3</sub> Br	Bromotrifluoromethane	340.20	39.70	0.1710
7.	R115	C <sub>2</sub> ClF <sub>5</sub>	Chloropentafluoroethane	353.20	32.30	0.2790
8.	R116	C <sub>2</sub> F <sub>6</sub>	Hexafluoroethane	293.00	30.60	0.2554
9.	R124	C <sub>2</sub> HClF <sub>4</sub>	1- Chloro- 1,2,2,2 -tetrafluoroethane	399.90	37.20	0.2810
10.	R125	C <sub>2</sub> H <sub>2</sub> F <sub>5</sub>	Pentafluoroethane	339.33	35.82	0.3035
11.	R134a	C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	1,1,1,2-Tetrafluoroethane	374.26	40.68	0.3261
12.	R142b	C <sub>2</sub> H <sub>3</sub> ClF <sub>2</sub>	1- Chloro- 1,1 -difluoroethane	409.60	43.30	0.2510
13.	R143a	C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	1,1,1 -Trifluoroethane	346.30	37.60	0.2510
14.	R152a	C <sub>2</sub> H <sub>4</sub> F <sub>2</sub>	1,1,1 -Difluoroethane	386.70	45.00	0.2560
15.	R236fa	C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	1,1,1,3,3,3 - Hexafluoropropane	398.07	31.58	
16.	R290	C <sub>3</sub> H <sub>8</sub>	Propane	369.80	42.50	0.2030
17.	R600a	C <sub>4</sub> H <sub>10</sub>	Isobutane	408.20	36.50	0.1830
18.	Propylene	C <sub>3</sub> H <sub>6</sub>	Propene	364.90	46.00	0.1440

**Table 5.3. Optimized UNIFAC group assignment for refrigerants**

Main	group	Subgroup	No.	R <sub>k</sub>	Q <sub>k</sub>
1	CH <sub>2</sub>	CH <sub>3</sub>	1	0.9011	0.848
		CH <sub>2</sub>	2	0.6744	0.540
		CH	3	0.4469	0.228
		C	4	0.2195	0.000
40	CF <sub>2</sub>	CF <sub>3</sub>	74	1.4060	1.380
		CF <sub>2</sub>	75	1.0105	0.920
		CF	76	0.6150	0.460
45	CF <sub>4</sub>	CF <sub>4</sub>	86	1.8016	1.840
51	CHF	CH <sub>3</sub> F	109	1.2966	1.308
		CH <sub>2</sub> F	110	1.0699	1.000
		CHF	111	0.8420	0.688
52	CHF <sub>2</sub>	CH <sub>2</sub> F <sub>2</sub>	112	1.4654	1.460
		CHF <sub>2</sub>	113	1.2380	1.232
		CH <sub>3</sub> - CHF <sub>2</sub>	114	2.1391	2.080
		(C F <sub>3</sub> -)CH <sub>2</sub> F	115	1.0699	1.000
53	CHF <sub>3</sub>	CHF <sub>3</sub>	116	1.6335	1.608
		(CH <sub>2</sub> -) CF <sub>3</sub>	117	1.4060	1.380
54	CClF	CCl <sub>3</sub> F	118	3.0356	2.644
		CCl <sub>2</sub> F	119	2.2446	1.920
55	CClF <sub>2</sub>	CCl <sub>2</sub> F <sub>2</sub>	120	2.5926	2.368
		CClF <sub>2</sub>	121	1.8016	1.644
		CBrF <sub>3</sub>	122	2.4028	2.232
56	CClF <sub>3</sub>	CCl F <sub>2</sub>	123	2.1971	2.104
		(CF <sub>3</sub> -) CCl F <sub>2</sub>	124	1.8016	1.644
		CClBrF <sub>2</sub>	125	2.4028	2.232

(Continued)

57	CHClF	CHClF <sub>2</sub>	126	2.0290	1.872
		(CH <sub>3</sub> -) CCl F <sub>2</sub>	127	1.8016	1.644
		CHClF	128	1.6335	1.412
58	CHCl <sub>2</sub> F	CHCl <sub>2</sub> F	129	2.4562	2.144
		CH <sub>3</sub> - CCl <sub>2</sub> F	130	3.1457	2.768
		CHCl <sub>2</sub> - CF <sub>3</sub>	131	3.6624	3.378
59	CF <sub>3</sub> Cl <sub>3</sub>	CFCl <sub>2</sub> - CF <sub>2</sub> Cl	132	4.0462	3.564

**Table 5.4. Optimized Modified UNIFAC group assignment for refrigerants**

Main	group	Subgroup	No.	R <sub>k</sub>	Q <sub>k</sub>
1	CH <sub>2</sub>	CH <sub>3</sub>	1	0.6325	1.0608
		CH <sub>2</sub>	2	0.6325	0.7081
		CH	3	0.6325	0.3554
		C	4	0.6325	0.0000
40	CF <sub>2</sub>	CF <sub>3</sub>	74	1.7874	1.7975
		CF <sub>2</sub>	75	1.0843	1.1801
		CF	76	0.3806	0.5841
70	CF <sub>4</sub>	CF <sub>4</sub>	148	1.5375	1.9920
71	CHF	CH <sub>3</sub> F	149	1.2962	1.3087
		CH <sub>2</sub> F	150	1.0685	1.0007
		CHF	151	0.9386	0.9700
72	CHF <sub>2</sub>	CH <sub>2</sub> F <sub>2</sub>	152	1.7529	1.8147
		CHF <sub>2</sub>	153	1.1396	1.4390
		CH <sub>3</sub> - CHF <sub>2</sub>	154	1.9820	2.3811
		(C F <sub>3</sub> -)CH <sub>2</sub> F	155	0.7108	1.1005
73	CHF <sub>3</sub>	CHF <sub>3</sub>	156	1.7272	1.9637
		(CH <sub>2</sub> -) CF <sub>3</sub>	157	1.4246	1.3487
74	CClF	CCl <sub>3</sub> F	158	2.6679	2.7843
		CCl <sub>2</sub> F	159	2.0418	2.0035
75	CClF <sub>2</sub>	CCl <sub>2</sub> F <sub>2</sub>	160	2.3591	3.0749
		CClF <sub>2</sub>	161	1.3574	1.7688
		CBrF <sub>3</sub>	162	2.2767	2.8122
76	CClF <sub>3</sub>	CCl F <sub>2</sub>	163	2.1347	2.0935
		(CF <sub>3</sub> -) CCl F <sub>2</sub>	164	1.0782	1.0584
		CClBrF <sub>2</sub>	165	1.9280	1.9139
77	CHClF	CHClF <sub>2</sub>	166	1.8552	2.0267
		(CH <sub>3</sub> -) CCl F <sub>2</sub>	167	1.6803	1.5016

(Continued)

		CHClF	168	1.4422	1.6403
78	CHCl <sub>2</sub> F	CHCl <sub>2</sub> F	169	2.2504	2.9420
		CH <sub>3</sub> - CCl <sub>2</sub> F	170	3.1638	2.8374
		CHCl <sub>2</sub> - CF <sub>3</sub>	171	2.2703	3.5910
79	CF <sub>3</sub> Cl <sub>3</sub>	CFCl <sub>2</sub> - CF <sub>2</sub> Cl	172	3.3963	4.3036

**Table 5.5. Average deviation in vapor – phase composition,  $(\Delta y)$  and pressure,  $(\Delta p/p)$  for systems**

S.No	System	Number of Data points N	Temp K	UNIFAC Method		Modified UNIFAC Method		Peng-Robinson with van der Waals Mixing Rules	
				$\Delta y'$	$\frac{\Delta p}{p}$	$\Delta y'$	$\frac{\Delta p}{p}$	$\Delta y'$	$\frac{\Delta p}{p}$
HCFC - HFC									
1.	R22 – R134a	7	273.15	0.0247	0.0381	0.0208	0.0402	0.0045	0.0261
		6	298.16	0.0218	0.0302	0.0162	0.0279	0.0059	0.0232
HCFC - HCFC									
2.	R22 – R142b	15	263.15	0.0357	0.0516	0.0338	0.0439	0.0161	0.0169
		16	273.15	0.0211	0.0519	0.0182	0.0421	0.0108	0.0136
		16	283.15	0.0265	0.0405	0.0255	0.0304	0.0059	0.0076
		21	293.15	0.0299	0.0418	0.0274	0.0301	0.0035	0.0087
3	R124 – R142b	12	298.15	0.0111	0.0328	0.0151	0.0438	0.0138	0.0342
		11	312.15	0.0149	0.0300	0.0178	0.0374	0.0176	0.0350
HFC - CFC									
4.	R32 – R12	16	283.15	0.0218	0.0334	0.0292	0.0516	0.0724	0.1933
5.	R134a – R12	10	258.00	0.0533	0.1402	0.0590	0.1529	0.0732	0.2044
		10	278.00	0.0456	0.1234	0.0515	0.1366	0.0634	0.1804

		10	298.00	0.0380	0.1093	0.0440	0.1230	0.0544	0.1575
HFC - HFC									
6.	R32 - R22	11	283.15	0.0169	0.0415	0.0171	0.0433	0.0838	0.2316
7.	R134a - R124	6	296.45	0.0205	0.0605	0.0083	0.0205	0.0097	0.0579
		9	302.25	0.02606	0.0629	0.0129	0.0272	0.0112	0.0609
		8	307.25	0.02015	0.0589	0.0093	0.0259	0.0077	0.0597
8.	R134a - R142b	10	268.00	0.0165	0.0613	0.0174	0.0302	0.0133	0.0348
		11	283.00	0.0148	0.0504	0.0221	0.0348	0.0140	0.0273
		11	298.00	0.0128	0.0445	0.0248	0.0358	0.0132	0.0234
HFC - HFC									
9.	R32 - R125	7	268.15	0.0078	0.0137	0.0312	0.0671	0.0093	0.0073
		7	278.15	0.0088	0.0151	0.0304	0.0577	0.0090	0.0086
10.	R32 - R134a	5	263.15	0.0248	0.0382	0.0568	0.1542	0.0091	0.0125
		5	273.15	0.0308	0.0458	0.0608	0.1513	0.0072	0.0139
		5	283.15	0.0335	0.0416	0.0558	0.1309	0.0100	0.0118
11.	R32 - R143a	10	263.15	0.0561	0.1157	0.0696	0.1589	0.0063	0.0209
		10	273.15	0.0519	0.1135	0.0631	0.1490	0.0098	0.0199
12.	R134a - R152a	8	255.00	0.0250	0.0864	0.0496	0.1702	0.0065	0.0314
		8	275.00	0.0246	0.0818	0.0421	0.1436	0.0049	0.0240
		9	298.00	0.0207	0.0729	0.0310	0.1114	0.0021	0.0184



(Continued)

13.	R134a – R236fa	9	283.62	0.0339	0.0786	0.0377	0.0906	0.0230	0.0959
		10	303.68	0.0349	0.0715	0.0403	0.0893	0.0145	0.0659
14.	R143a – R134a	9	263.15	0.0199	0.0138	0.0217	0.0275	0.0075	0.0080
		9	273.15	0.0325	0.0103	0.0344	0.0238	0.0174	0.0049
		9	283.15	0.0234	0.0134	0.0236	0.0268	0.0054	0.0058
HFC - FC									
15.	R23 – R116	12	209.60	0.0249	0.0459	0.0642	0.0811	0.0998	0.2137
16.	R134a – R116	10	251.00	0.0554	0.2084	0.0703	0.2481	0.0859	0.2635
BrFC - CFC									
17.	R13B1 – R13	8	255.00	0.0470	0.0981	0.0318	0.0500	0.0128	0.0299
HFC - HC									
18.	R134a – R290	9	255.00	0.0790	0.1975	0.0481	0.1390	0.1452	0.3080
		9	275.00	0.0612	0.1649	0.0305	0.1051	0.1225	0.2708
		11	298.00	0.0430	0.1287	0.0161	0.0713	0.0998	0.2225
19.	R134a – R600a	17	293.66	0.0647	0.1570	0.0439	0.1197	0.1421	0.2788
		11	303.68	0.0466	0.1297	0.0295	0.0947	0.1141	0.2442
HFC - HOC									
20.	R134a – Dimethyl ether	10	258.00	0.0789	0.3052	0.0375	0.0441	0.0434	0.1194
		8	298.00	0.0735	0.2323	0.0189	0.0456	0.0202	0.0618

HCFC - HOC										
21.	R142b – Dimethyl ether	11	268.00	0.0189	0.0771	0.0118	0.0531	0.0249	0.0649	
		10	298.00	0.0232	0.0775	0.0139	0.0403	0.0190	0.0612	
HC - CFC										
22.	Propylene – R12	9	258.00	0.0050	0.0060	0.0079	0.0185	0.0108	0.0633	
		9	263.00	0.0060	0.0261	0.0077	0.0219	0.0104	0.0623	
		9	268.00	0.0092	0.0187	0.0084	0.0200	0.0099	0.0589	
		9	273.00	0.0121	0.0251	0.0108	0.0213	0.0113	0.0574	
		9	278.00	0.0172	0.0313	0.0123	0.0223	0.0109	0.0553	
		9	283.00	0.0215	0.0392	0.0121	0.0395	0.0079	0.0525	
23.	Propylene – R13	10	251.00	0.0427	0.0254	0.0650	0.1458	0.0329	0.1348	
24.	Propylene – R115	8	251.00	0.0099	0.0127	0.0263	0.0423	0.0575	0.1404	
		8	275.00	0.0150	0.0094	0.0465	0.0659	0.0410	0.1112	
HC - HCFC										
25.	Propylene – R22	8	258.00	0.0091	0.0096	0.0076	0.0198	0.0205	0.0606	
		8	263.00	0.0067	0.0116	0.0086	0.0188	0.0203	0.0605	
		8	268.00	0.0067	0.0127	0.0085	0.0183	0.0197	0.0595	
		7	273.00	0.0102	0.0122	0.0054	0.0168	0.0175	0.0568	
		8	278.00	0.0091	0.0130	0.0058	0.0171	0.0192	0.0548	
		8	283.00	0.0115	0.0131	0.0054	0.0172	0.0189	0.0535	

(Continued)

26.	Propylene - R142b	7	268.00	0.0143	0.0144	0.0122	0.0271	0.0151	0.0537
		7	278.00	0.0165	0.0103	0.0146	0.0197	0.0211	0.0524
		9	288.00	0.0147	0.0049	0.0129	0.0120	0.0265	0.0452
		8	298.00	0.0258	0.0115	0.0240	0.0130	0.0262	0.0407
HC - HFC									
27.	R600a - R236fa	15	303.68	0.0406	0.1263	0.0431	0.0433	0.1070	0.2076
28.	Propylene - R134a	9	251.00	0.0309	0.0825	0.0500	0.1265	0.0945	0.2124
		10	275.00	0.0190	0.0671	0.0230	0.0805	0.0716	0.1884
29.	Propylene - R152a	9	255.00	0.0083	0.0102	0.0164	0.0392	0.0669	0.1608
		9	265.00	0.0085	0.0207	0.0158	0.0438	0.0627	0.1538
		9	275.00	0.0164	0.0076	0.0167	0.0317	0.0579	0.1459
		9	285.00	0.0254	0.0137	0.0214	0.0317	0.04724	0.1360
HC - FC									
30.	Propylene - R116	9	251.00	0.0317	0.0435	0.0320	0.0501	0.1002	0.1865
HC - BrFC									
31.	Propylene - R133i	8	251.00	0.0164	0.0332	0.0190	0.0079	0.0149	0.0603
		8	275.00	0.0216	0.0012	0.0244	0.0074	0.0116	0.0537

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**Table 5.6: VLE Data for R22 (1) – R134a (2)**

**Temperature: 273.16 K**

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	$x_1$	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)
1	0.0000	0.0000	2.9250	0.0000	2.9250	0.0000	2.9250	0.0000	2.9259
2	0.3035	0.4209	3.6400	0.4327	3.3903	0.4600	3.8398	0.4126	3.5326
3	0.4128	0.5304	3.9350	0.5680	3.6668	0.5662	4.1051	0.5305	3.7516
4	0.5759	0.6847	4.1900	0.7240	4.0836	0.6965	4.4407	0.6848	4.0790
5	0.7386	0.8122	4.5100	0.8408	4.4629	0.8088	4.7069	0.8181	4.4066
6	0.8240	0.8750	4.67500	0.8937	4.6437	0.8664	4.8198	0.8814	4.5789
7	1.0000	1.0000	4.9830	1.0000	4.9830	1.0000	4.9830	1.0000	4.9354
$\overline{\Delta y}$				0.0247		0.0208		0.0045	
$\overline{\Delta p}/p$					0.0381		0.0402		0.0261

**Table 5.7: VLE Data for R22 (1) – R142b (2)**

**Temperature: 263.15 K**

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>1</sub>	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)
1	0.0000	0.0000	0.9800	0.0000	0.9800	0.0000	0.9800	0.0000	1.0025
2	0.0680	0.1550	1.1200	0.2278	1.1834	0.2221	1.1745	0.1941	1.1661
3	0.1010	0.2460	1.2100	0.3109	1.2798	0.3045	1.2675	0.2704	1.2459
4	0.2650	0.5390	1.6100	0.5827	1.7396	0.5786	1.7176	0.5421	1.6456
5	0.3940	0.6460	1.9300	0.7094	2.0807	0.708	2.0579	0.6802	1.9643
6	0.4480	0.7130	2.0800	0.7503	2.2190	0.7498	2.1970	0.7261	2.0988
7	0.5230	0.7710	2.2700	0.7992	2.4071	0.7996	2.3871	0.7813	2.2868
8	0.5430	0.7850	2.3200	0.8109	2.4566	0.8116	2.4373	0.7946	2.3372
9	0.5730	0.8020	2.4000	0.8276	2.5303	0.8286	2.5122	0.8136	2.4129
10	0.6310	0.8460	2.5500	0.8575	2.6714	0.8588	2.6557	0.8474	2.5599
11	0.6660	0.8690	2.6400	0.8741	2.7558	0.8755	2.7415	0.8661	2.6491
12	0.7120	0.8930	2.7600	0.8946	2.8659	0.8961	2.8537	0.8890	2.7667
13	0.7900	0.9320	2.9800	0.9264	3.0512	0.9278	3.0426	0.9240	2.9675
14	0.9340	0.9830	3.3600	0.9782	3.3923	0.9789	3.3897	0.9785	3.3427
15	1.0000	1.0000	3.5500	1.0000	3.5500	1.0000	3.5500	1.0000	3.5166
$\Delta y$				0.0357		0.0338		0.0161	
$\Delta p/p$					0.0516		0.0439		0.0169

**Table 5.8: VLE Data for R124 (1) – R142b (2)**

**Temperature: 298.15 K**

Experimental			UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>1</sub>	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	P (bar)
1	0.0000	0.0000	3.3800	0.0000	3.3800	0.0000	3.3800	3.5103
2	0.0390	0.0410	3.3900	0.0499	3.4194	0.0549	3.4392	3.5157
3	0.0500	0.0530	3.3900	0.0635	3.4301	0.0695	3.4545	3.5172
4	0.1890	0.1960	3.4300	0.2231	3.5485	0.2301	3.6066	3.5336
5	0.2400	0.2630	3.4500	0.2769	3.5851	0.2818	3.6476	3.5386
6	0.4310	0.4520	3.5100	0.4640	3.6937	0.4602	3.7544	3.5535
7	0.5400	0.5660	3.5600	0.5649	3.7375	0.5582	3.7896	3.5592
8	0.5870	0.6110	3.5900	0.6078	3.7527	0.6006	3.8001	3.5610
9	0.6840	0.7030	3.6200	0.6964	3.7770	0.6891	3.8135	3.5638
10	0.7830	0.8000	3.6900	0.7879	3.7921	0.7821	3.8167	3.5651
11	0.9470	0.9490	3.7700	0.9461	3.7952	0.9447	3.8006	3.5643
12	1.0000	1.0000	3.7900	1.0000	3.7900	1.0000	3.7900	3.5632
$\overline{\Delta y}$				0.0111		0.0151		0.0138
$\overline{\Delta p}/p$					0.0328		0.0438	0.0342

**Table 5.9: VLE Data for R134a (1) – R12 (2)**

**Temperature: 258.0 K**

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>1</sub>	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)
1	0.0000	0.0000	1.8150	0.0000	1.8150	0.0000	1.8150	0.0000	1.6996
2	0.1222	0.2152	2.0790	0.1348	1.8527	0.1258	1.8274	0.1181	1.6912
3	0.2451	0.3221	2.1970	0.2493	1.8667	0.2429	1.8297	0.2379	1.6827
4	0.3213	0.3747	2.2310	0.3155	1.8664	0.3127	1.8264	0.3128	1.6774
5	0.4893	0.4638	2.2440	0.4586	1.8459	0.4639	1.8068	0.4794	1.6657
6	0.5476	0.5005	2.2320	0.5094	1.8329	0.5168	1.7960	0.5377	1.6616
7	0.6515	0.5594	2.1860	0.6043	1.8026	0.6138	1.7716	0.6424	1.6543
8	0.7623	0.6421	2.0990	0.7141	1.7600	0.7233	1.7374	0.7550	1.6466
9	0.8680	0.7542	1.9480	0.8309	1.7091	0.8374	1.6963	0.8633	1.6391
10	1.0000	1.0000	1.6310	1.0000	1.6310	1.0000	1.6310	1.0000	1.6298
$\Delta y$				0.0533		0.0590		0.0732	
$\Delta p / p$					0.1402		0.1529		0.2044

**Table 5.10: VLE Data for R134a (1) – R124 (2)**

**Temperature: 296.45 K**

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>1</sub>	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)
1	0.00000	0.00000	3.70000	0.00000	3.70000	0.00000	3.70000	0.00000	3.37850
2	0.19300	0.29700	4.21000	0.25830	4.00730	0.28630	4.18330	0.29350	3.92350
3	0.40900	0.54200	4.85000	0.51930	4.43240	0.53730	4.72520	0.54500	4.54570
4	0.55800	0.66300	5.27000	0.67770	4.79050	0.67940	5.09940	0.68540	4.98300
5	0.75500	0.83500	5.72000	0.85230	5.36170	0.83810	5.59430	0.84120	5.57200
6	1.00000	1.00000	6.21000	1.00000	6.21000	1.00000	6.21000	1.00000	6.32260
$\Delta y$				0.0205		0.0083		0.0097	
$\Delta p / p$					0.0605		0.0205		0.0579



Table 5.11: VLE Data for R134a (1) – R142b (2)

Temperature: 268.0 K

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>1</sub>	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)
1	0.0000	0.0000	1.1890	0.0000	1.1890	0.0000	1.1890	0.0000	1.2190
2	0.1820	0.3275	1.4810	0.3040	1.4059	0.3651	1.5559	0.3010	1.4381
3	0.2735	0.4448	1.6200	0.4188	1.5038	0.4734	1.6962	0.4206	1.5478
4	0.3737	0.5423	1.7530	0.5288	1.6080	0.5677	1.8288	0.5339	1.6675
5	0.4695	0.6359	1.8740	0.6237	1.7084	0.6442	1.9409	0.6285	1.7819
6	0.5720	0.7089	1.9960	0.7171	1.8211	0.7175	2.0494	0.7178	1.9042
7	0.7013	0.8045	2.1320	0.8239	1.9776	0.8037	2.1739	0.8162	2.0587
8	0.8371	0.8965	2.2720	0.9195	2.1674	0.8918	2.2936	0.9062	2.2213
9	0.9495	0.9664	2.3730	0.9800	2.3441	0.9658	2.3856	0.9723	2.3566
10	1.0000	1.0000	2.4250	1.0000	2.4250	1.0000	2.4250	1.0000	2.4176
$\overline{\Delta y}$				0.0165		0.0174		0.0133	
$\overline{\Delta p}/p$					0.0613		0.0302		0.0348

Table 5.12: VLE Data for R32 (1) – R125 (2)

Temperature: 268 . 15 K

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	$x_1$	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)
1	0.0000	0.0000	5.7130	0.0000	5.7130	0.0000	5.7130	0.0000	5.6142
2	0.1996	0.2282	6.0680	0.2421	6.0470	0.2825	6.4049	0.2480	6.0703
3	0.3494	0.3979	6.3430	0.4027	6.2717	0.4453	6.8381	0.4075	6.3649
4	0.4929	0.5363	6.5880	0.5440	6.4645	0.5729	7.1619	0.5451	6.6031
5	0.6265	0.6578	6.7670	0.6675	6.6229	0.6734	7.3642	0.6641	6.7813
6	0.7323	0.7542	6.8660	0.7618	6.7327	0.7453	7.4421	0.7553	6.8886
7	1.0000	1.0000	6.9380	1.0000	6.9380	1.0000	6.9380	1.0000	6.9828
$\overline{\Delta y}$				0.0078		0.0312		0.0093	
$\overline{\Delta p}/p$					0.0137		0.0671		0.0073

**Table 5.13: VLE Data for R134a (1) – R152a (2)**

**Temperature: 255.0 K**

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	$x_1$	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)
1	0.0000	0.0000	1.3060	0.0000	1.3060	0.0000	1.3060	0.0000	1.3559
2	0.3147	0.3298	1.3280	0.3685	1.4677	0.3767	1.6430	0.3277	1.3848
3	0.4489	0.4659	1.3420	0.4842	1.5000	0.4586	1.6630	0.4630	1.3962
4	0.5495	0.5737	1.3540	0.5659	1.5129	0.5250	1.6593	0.5631	1.4044
5	0.6580	0.6736	1.3710	0.6542	1.5162	0.6070	1.6377	0.6698	1.4130
6	0.7594	0.7777	1.3890	0.7412	1.5087	0.6975	1.6000	0.7686	1.4207
7	0.8843	0.8998	1.4140	0.8623	1.4830	0.8353	1.5291	0.8892	1.4299
8	1.0000	1.0000	1.4380	1.0000	1.4380	1.0000	1.4380	1.0000	1.4381
$\Delta y$				0.0250		0.0496		0.0065	
$\frac{\Delta p}{p}$					0.0864		0.1702		0.0314

**Table 5.14: VLE Data for R143a (1) – R134a (2)**

**Temperature: 263.15 K**

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	$x_1$	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)
1	0.0000	0.0000	2.0010	0.0000	2.0010	0.0000	2.0010	0.0000	2.0053
2	0.0834	0.1522	2.2190	0.1648	2.1919	0.1813	2.2410	0.1656	2.2184
3	0.1999	0.3449	2.4980	0.3620	2.4889	0.3754	2.5683	0.3499	2.5126
4	0.3629	0.5396	2.8740	0.5713	2.9262	0.5725	3.0078	0.5466	2.9190
5	0.5208	0.6878	3.2700	0.7176	3.3434	0.7125	3.4102	0.6933	3.3094
6	0.6520	0.7796	3.6000	0.8115	3.6752	0.8051	3.7265	0.7934	3.6332
7	0.7957	0.8811	3.9590	0.8963	4.0231	0.8912	4.0555	0.8871	3.9893
8	0.9214	0.9592	4.2930	0.9615	4.3183	0.9589	4.3316	0.9588	4.3037
9	1.0000	1.0000	4.5010	1.0000	4.5010	1.0000	4.5010	1.0000	4.5024
$\Delta y$				0.0199		0.0217		0.0075	
$\Delta p / p$					0.0138		0.0275		0.0080

Table 5.16: VLE Data for R13B1 (1) – R13 (2)

Temperature: 255.00 K

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	$x_1$	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)	$y_1$	P (bar)
1	0.0000	0.0000	12.0660	0.0000	12.0660	0.0000	12.0660	0.0000	11.7418
2	0.2240	0.1227	10.4400	0.1293	11.0415	0.1167	10.7647	0.1272	10.0793
3	0.4031	0.2446	9.1860	0.2259	10.0869	0.2200	9.6487	0.2499	8.8140
4	0.5360	0.3450	8.2230	0.3069	9.2637	0.3118	8.7550	0.3594	7.9020
5	0.6864	0.4900	7.1280	0.4249	8.1544	0.4452	7.6492	0.5111	6.8912
6	0.7778	0.6032	6.4630	0.5233	7.3554	0.5522	6.9137	0.6235	6.2860
7	0.9049	0.8025	5.5330	0.7303	6.0380	0.7605	5.7902	0.8164	5.4539
8	1.0000	1.0000	4.8570	1.0000	4.8570	1.0000	4.8570	1.0000	4.8374
$\overline{\Delta y}$				0.0470		0.0318		0.0128	
$\Delta p / p$					0.0981		0.0500		0.0299

Table 5.17: VLE Data for R134a (1) – R600a (2)

Temperature: 293.66 K

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>1</sub>	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)
1	0.0000	0.0000	3.0670	0.0000	3.0670	0.0000	3.0670	0.0000	3.0526
2	0.0626	0.2822	4.2610	0.1951	3.5803	0.2234	3.7136	0.1060	3.2178
3	0.0970	0.3805	4.7320	0.2719	3.8261	0.3044	4.0118	0.1601	3.3089
4	0.0982	0.3751	4.7010	0.2743	3.8342	0.3069	4.0215	0.1619	3.3121
5	0.1082	0.3853	4.7850	0.2938	3.9011	0.3267	4.1011	0.1771	3.3386
6	0.1238	0.4173	4.9500	0.3220	4.0016	0.3552	4.2196	0.2003	3.3801
7	0.1953	0.4933	5.5240	0.4265	4.4093	0.4562	4.6844	0.3006	3.5708
8	0.2289	0.5182	5.6910	0.4651	4.5738	0.4920	4.8642	0.3444	3.6608
9	0.2969	0.5608	6.0190	0.5298	4.8620	0.5499	5.1668	0.4273	3.8438
10	0.4526	0.6241	6.4360	0.6371	5.3443	0.6416	5.6334	0.5929	4.2670
11	0.5284	0.6481	6.5540	0.6786	5.5124	0.6763	5.7824	0.6634	4.4753
12	0.5680	0.6607	6.6180	0.6990	5.5868	0.6935	5.8457	0.6979	4.5847
13	0.6513	0.6903	6.6660	0.7412	5.7173	0.7297	5.9512	0.7662	4.8161
14	0.7442	0.7295	6.6900	0.7906	5.8238	0.7741	6.0261	0.8359	5.0763
15	0.7977	0.7579	6.6550	0.8222	5.8650	0.8043	6.0451	0.8733	5.2273
16	0.9028	0.8427	6.4140	0.8982	5.8883	0.8826	6.0038	0.9419	5.5262
17	1.0000	1.0000	5.8000	1.0000	5.8000	1.0000	5.8000	1.0000	5.8056
$\bar{\Delta y}$				0.0647		0.0439		0.1421	
$\frac{\Delta p}{p}$					0.1570		0.1197		0.2788

**Table 5.18: VLE Data for R134a (1) – Dimethyl ether (2)**

**Temperature: 258.00 K**

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>1</sub>	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)
1	1.0000	1.0000	1.6280	1.0000	1.6280	1.0000	1.6280	1.0000	1.6298
2	0.6569	0.7096	1.4300	0.8245	0.9785	0.6667	1.4172	0.6720	1.6017
3	0.6271	0.6832	1.4170	0.7820	0.9367	0.6285	1.4158	0.6435	1.5984
4	0.5629	0.6088	1.3900	0.6698	0.8682	0.5478	1.4191	0.5821	1.5906
5	0.4608	0.4722	1.3630	0.4513	0.8292	0.4281	1.4361	0.4835	1.5767
6	0.4454	0.4577	1.3640	0.4174	0.8314	0.4112	1.4395	0.4685	1.5744
7	0.3154	0.2912	1.3750	0.1735	0.9334	0.2797	1.4707	0.3397	1.5532
8	0.2839	0.2422	1.3890	0.1319	0.9790	0.2505	1.4783	0.3078	1.5475
9	0.2710	0.2039	1.3930	0.1170	0.9997	0.2388	1.4814	0.2947	1.5451
10	0.0000	0.0000	1.5290	0.0000	1.5290	0.0000	1.5290	0.0000	1.4839
$\overline{\Delta y}$				0.0789		0.0375		0.0434	
$\overline{\Delta p/p}$					0.3052		0.0441		0.1194

Table 5.19: VLE Data for R142b (1) – Dimethyl ether (2)

Temperature: 268.0K

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>1</sub>	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)	y <sub>1</sub>	P (bar)
1	1.0000	1.0000	1.1830	1.0000	1.1830	1.0000	1.1830	1.0000	1.2190
2	0.7748	0.6955	1.3160	0.7369	1.1974	0.7204	1.2357	0.6631	1.4356
3	0.7149	0.6383	1.3580	0.6510	1.2222	0.6366	1.2676	0.5897	1.4929
4	0.6247	0.5004	1.4410	0.5192	1.2799	0.5111	1.3319	0.4889	1.5791
5	0.5514	0.4131	1.5110	0.4163	1.3457	0.4142	1.3991	0.4146	1.6489
6	0.4753	0.3318	1.5970	0.3185	1.4319	0.3219	1.4830	0.3435	1.7212
7	0.3464	0.2049	1.7580	0.1826	1.6158	0.1907	1.6558	0.2353	1.8434
8	0.2349	0.1203	1.9110	0.0976	1.8050	0.1051	1.8310	0.1518	1.9488
9	0.2026	0.0973	1.9550	0.0782	1.8632	0.0850	1.8850	0.1292	1.9794
10	0.0921	0.0405	2.1010	0.0274	2.0663	0.0306	2.0746	0.0562	2.0837
11	0.0000	0.0000	2.2300	0.0000	2.2300	0.0000	2.2300	0.0000	2.1707
$\Delta y$				0.0189		0.0118		0.0249	
$\frac{\Delta p}{p}$					0.0771		0.0531		0.0649



**Table 5.20: VLE Data for Propylene (1) – R12 (2)**  
**Temperature: 258.0 K**

Experimental			UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>2</sub>	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	y <sub>2</sub>	P (bar)
1	0.0000	0.0000	3.6240	0.0000	3.6240	0.0000	0.0000	3.5966
2	0.0940	0.0594	3.4900	0.0558	3.4717	0.0608	0.0496	3.4120
3	0.1717	0.1091	3.3780	0.1059	3.3510	0.1110	0.0942	3.2605
4	0.2963	0.1857	3.2000	0.1894	3.1624	0.1927	0.1742	3.0195
5	0.4255	0.2843	2.9790	0.2811	2.9645	0.2817	0.2703	2.7720
6	0.5246	0.3643	2.8000	0.3578	2.8051	0.3560	0.3553	2.5838
7	0.6476	0.4705	2.5870	0.4667	2.5913	0.4608	0.4781	2.3522
8	0.7609	0.5969	2.3530	0.5894	2.3726	0.5788	0.6130	2.1406
9	1.0000	1.0000	1.8130	1.0000	1.8130	1.0000	1.0000	1.6996
$\Delta y$				0.0050		0.0079	0.0108	
$\Delta p / p$					0.0060		0.0185	0.0633

Table 5.21: VLE Data for Propylene (1) – R115 (2)

Temperature: 251.0 K

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>2</sub>	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)
1	0.0000	0.0000	2.8830	0.0000	2.8830	0.0000	2.8830	0.0000	2.8219
2	0.1274	0.1696	3.0900	0.1776	3.1664	0.2046	3.2843	0.1002	2.7353
3	0.2123	0.2394	3.1420	0.2318	3.2067	0.2524	3.3412	0.1679	2.6736
4	0.4511	0.3753	3.1030	0.3523	3.1368	0.3348	3.2953	0.3707	2.4840
5	0.6267	0.4765	2.9490	0.4649	2.9446	0.4283	3.0848	0.5399	2.3302
6	0.8470	0.6956	2.5270	0.6976	2.5015	0.6849	2.5056	0.7904	2.1209
7	0.9337	0.8460	2.2690	0.8459	2.2573	0.8534	2.2281	0.9048	2.0338
8	1.0000	1.0000	2.0420	1.0000	2.0420	1.0000	2.0420	1.0000	1.9654
$\overline{\Delta y}$				0.0099		0.0263		0.0575	
$\frac{\Delta p}{p}$					0.0127		0.0423		0.1404

Table 5.22: VLE Data for Propylene (1) – R22 (2)

Temperature: 258.0 K

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>2</sub>	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)
1	0.0000	0.0000	3.6240	0.0000	3.6240	0.0000	3.6240	0.0000	3.5966
2	0.1867	0.1862	3.6700	0.1885	3.7258	0.1777	3.5809	0.1609	3.4770
3	0.2535	0.2438	3.6690	0.2416	3.7205	0.2416	3.5665	0.2206	3.4337
4	0.3367	0.3169	3.6490	0.3057	3.6952	0.3199	3.5469	0.2967	3.3792
5	0.3930	0.3617	3.6310	0.3492	3.6680	0.3718	3.5316	0.3495	3.3420
6	0.6170	0.5540	3.4870	0.5375	3.4891	0.5703	3.4392	0.5702	3.1914
7	0.8483	0.7833	3.2180	0.7855	3.1966	0.7862	3.2389	0.8204	3.0305
8	1.0000	1.0000	2.9490	1.0000	2.9490	1.0000	2.9490	1.0000	2.9213
$\overline{\Delta y}$				0.0091		0.0076		0.0205	
$\overline{\Delta p}/p$					0.0096		0.0198		0.0606

**Table 5.23: VLE Data for Propylene (1) – R142b (2)**

**Temperature: 268.0 K**

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>2</sub>	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)
1	0.0000	0.0000	4.9920	0.0000	4.9920	0.0000	4.9920	0.0000	4.9700
2	0.2739	0.1004	4.0900	0.0852	4.0542	0.0846	3.9938	0.0951	3.8977
3	0.3775	0.1478	3.6890	0.1260	3.6827	0.1271	3.6144	0.1432	3.5042
4	0.5026	0.1940	3.2800	0.1888	3.2147	0.1920	3.1488	0.2158	3.0355
5	0.6085	0.2682	2.8900	0.2599	2.8029	0.2648	2.7462	0.2954	2.6432
6	0.7191	0.3881	2.3410	0.3630	2.3594	0.3695	2.3162	0.4061	2.2371
7	1.0000	1.0000	1.1890	1.0000	1.1870	1.0000	1.1870	1.0000	1.2190
$\overline{\Delta y}$				0.0143		0.0122		0.0151	
$\overline{\Delta p}/p$					0.0144		0.0271		0.0537

Table 5.23: VLE Data for Propylene (1) – R134a (2)

Temperature: 251.0 K

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>2</sub>	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)
1	0.0000	0.0000	2.8330	0.0000	2.8330	0.0000	2.8330	0.0000	2.8219
2	0.1924	0.1728	2.9410	0.1407	2.7520	0.1232	2.6601	0.0974	2.5032
3	0.3397	0.2377	2.8820	0.2164	2.6345	0.2067	2.5031	0.1887	2.2623
4	0.4476	0.2762	2.7920	0.2682	2.5245	0.2685	2.3729	0.2678	2.0874
5	0.5221	0.2971	2.7240	0.3059	2.4338	0.3142	2.2732	0.3300	1.9673
6	0.7300	0.4134	2.3660	0.4460	2.0828	0.4763	1.9310	0.5485	1.6354
7	0.8478	0.5308	2.0110	0.5847	1.7821	0.6221	1.6708	0.7141	1.4492
8	0.9530	0.7618	1.5160	0.8164	1.4145	0.8417	1.3718	0.9008	1.2840
9	1.0000	1.0000	1.2100	1.0000	1.2100	1.0000	1.2100	1.0000	1.2106
$\Delta y$				0.0309		0.0500		0.0945	
$\frac{\Delta p}{p}$					0.0825		0.1265		0.2124

Table 5.25: VLE Data for Propylene (1) – R152a (2)

Temperature: 255.0 K

Experimental value of R152a				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	$x_2$	$y_2$	P (bar)	$y_2$	P (bar)	$y_2$	P (bar)	$y_2$	P (bar)
1	0.0000	0.0000	3.2610	0.0000	3.2610	0.0000	3.2610	0.0000	3.2471
2	0.1006	0.0900	3.2870	0.0864	3.2471	0.0737	3.1795	0.0479	3.0520
3	0.1780	0.1392	3.2490	0.1342	3.2048	0.1258	3.1086	0.0884	2.9031
4	0.3143	0.2073	3.1370	0.1996	3.0932	0.2096	2.9683	0.1694	2.6429
5	0.4390	0.2608	3.0010	0.2521	2.9569	0.2799	2.8239	0.2571	2.4067
6	0.5763	0.3222	2.7910	0.3152	2.7561	0.3543	2.6451	0.3742	2.1482
7	0.7053	0.4125	2.4990	0.3955	2.4896	0.4283	2.4464	0.5112	1.9063
8	0.8497	0.5622	2.0540	0.5521	2.0428	0.5444	2.1286	0.7106	1.6364
9	1.0000	1.0000	1.3050	1.0000	1.3050	1.0000	1.3050	1.0000	1.3559
$\overline{\Delta y}$				0.0083		0.0164		0.0669	
$\Delta p / p$					0.0102		0.0392		0.1608

**Table 5.26: VLE Data for Propylene (1) – R116 (2)**

**Temperature: 251.00 K**

Experimental			UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>2</sub>	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	P (bar)
1	0.0000	0.0000	2.8350	0.0000	2.8350	0.0000	0.0000	2.8219
2	0.0154	0.2152	3.5590	0.1933	3.4620	0.2321	3.6377	2.9692
3	0.0358	0.3386	4.3970	0.3443	4.1792	0.3898	4.4962	3.1594
4	0.5295	0.7230	9.3240	0.7690	8.7799	0.7543	8.6254	6.7776
5	0.6200	0.7456	9.5860	0.7933	9.0392	0.7829	8.8953	7.3542
6	0.6982	0.7783	9.7910	0.8185	9.2531	0.8128	9.1252	7.8528
7	0.7973	0.8230	9.9850	0.8595	9.5039	0.8599	9.3995	8.4938
8	0.8363	0.8445	10.0170	0.8794	9.5912	0.8817	9.4978	8.7507
9	1.0000	1.0000	9.8040	1.0000	9.8040	1.0000	9.8040	9.8738
$\Delta y$			0.0317		0.0320		0.1002	
$\frac{\Delta p}{p}$			0.0435		0.0501		0.1865	

Table 5.27: VLE Data for Propylene (1) – R13B1 (2)

Temperature: 251.0 K

Experimental				UNIFAC Method		Modified UNIFAC Method		P-R EOS with vdW one fluid Mixing Rule	
S.No	x <sub>2</sub>	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)	y <sub>2</sub>	P (bar)
1	0.0000	0.0000	2.8330	0.0000	2.8330	0.0000	2.8330	0.0000	2.8219
2	0.1124	0.1812	3.1350	0.1730	3.0283	0.1988	3.1493	0.1586	2.9926
3	0.1962	0.2897	3.3540	0.2909	3.1905	0.3130	3.3513	0.2651	3.1169
4	0.3018	0.4019	3.5530	0.4185	3.3882	0.4310	3.5703	0.3877	3.2705
5	0.4176	0.5115	3.7330	0.5362	3.5852	0.5385	3.7711	0.5099	3.4357
6	0.5596	0.6327	3.9170	0.6595	3.7961	0.6521	3.9690	0.6458	3.6343
7	0.6583	0.7156	4.0250	0.7374	3.9248	0.7251	4.0786	0.7328	3.7704
8	1.0000	1.0000	4.2740	1.0000	4.2740	1.0000	4.2740	1.0000	4.2334
$\Delta y$				0.0164		0.0190		0.0149	
$\frac{\Delta p}{p}$					0.0332		0.0079		0.0603



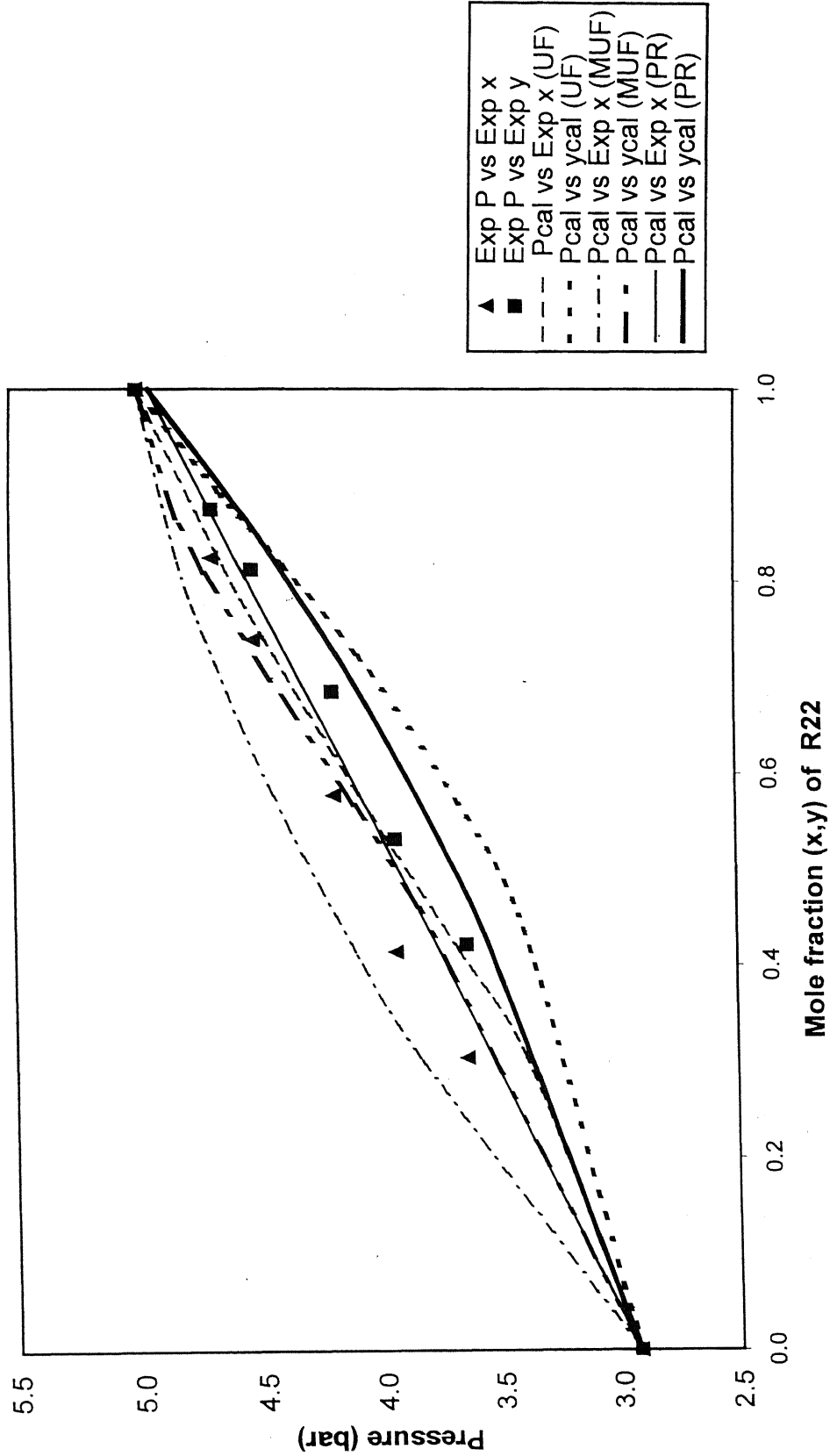


Figure 5.1. P-x-y diagram for R22 (1) / R134a (2) system at T=273.15 K

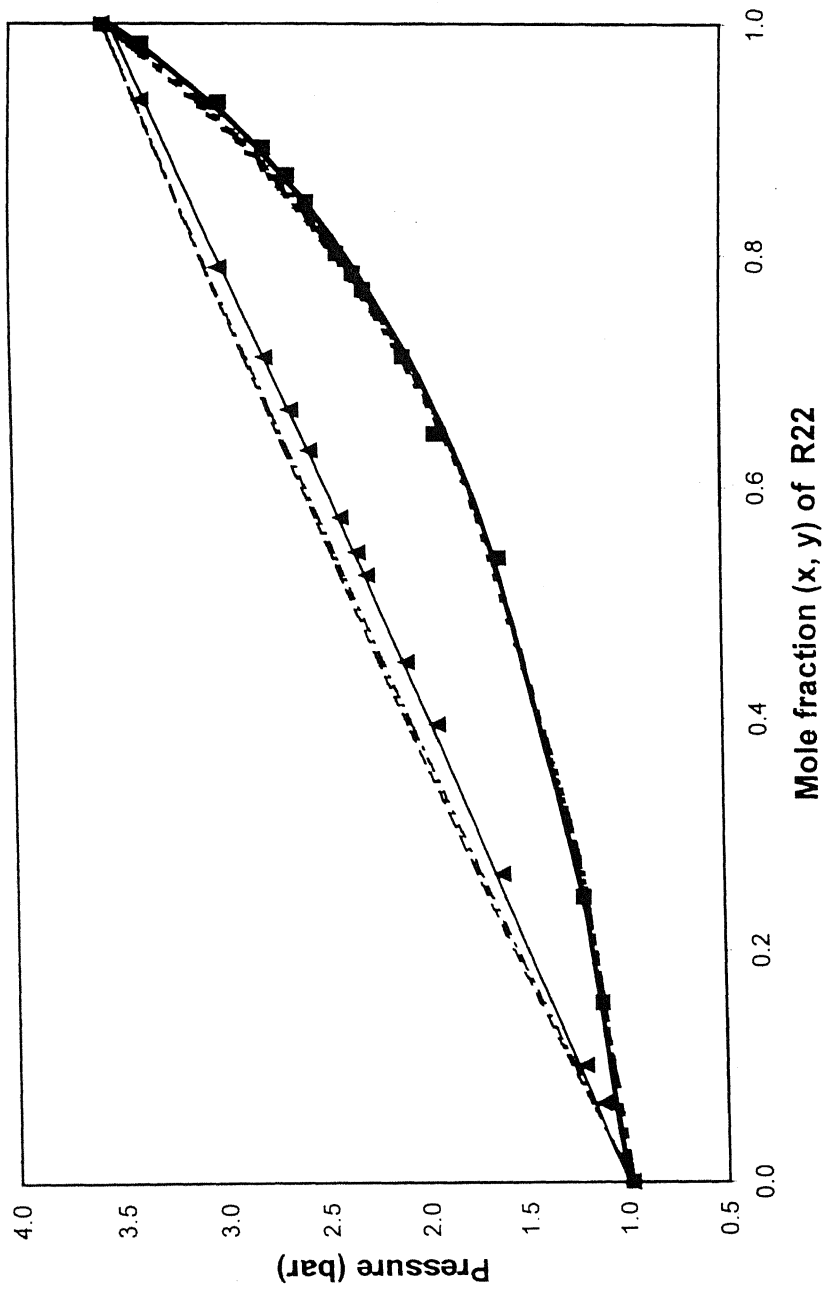


Figure 5.2. P-x-y diagram for R22 (1) / R142b (2) system at T=263.15 K

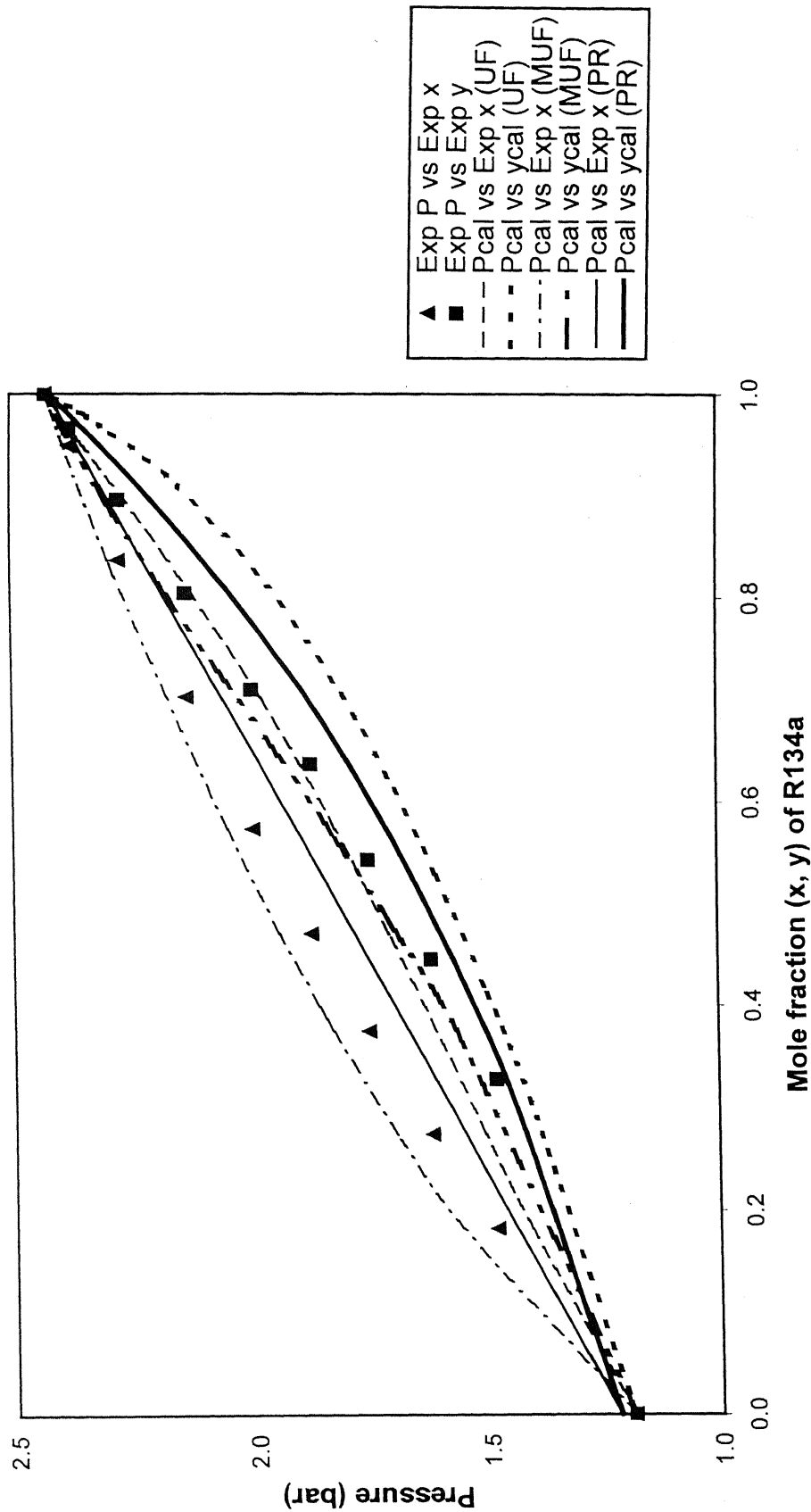


Figure 5.3. P-x-y diagram for R134a (1) / R142b (2) system at T=268.0 K

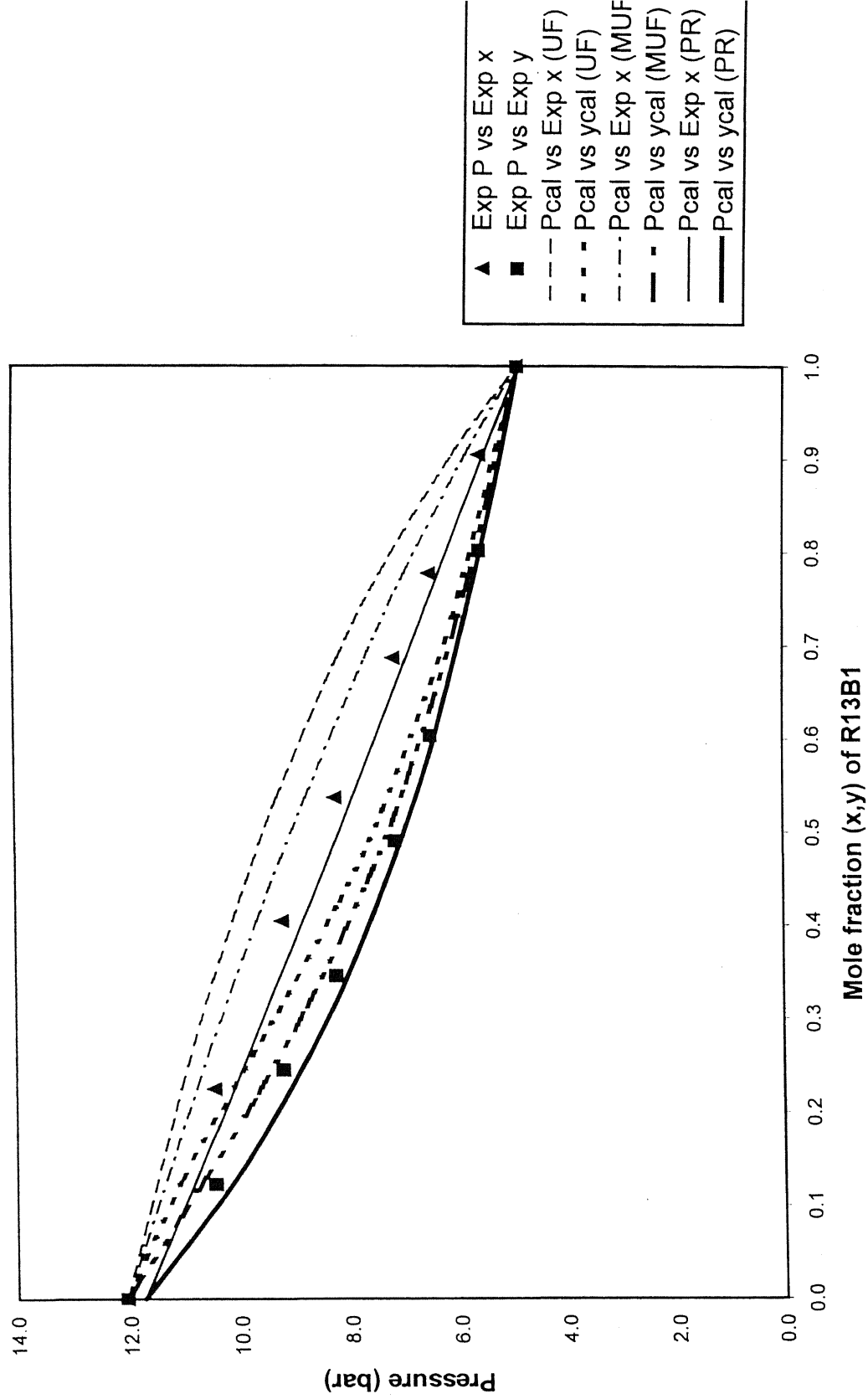


Figure 5.4. P-x-y diagram for R13B1 (1) / R13 (2) system at T=255.0 K

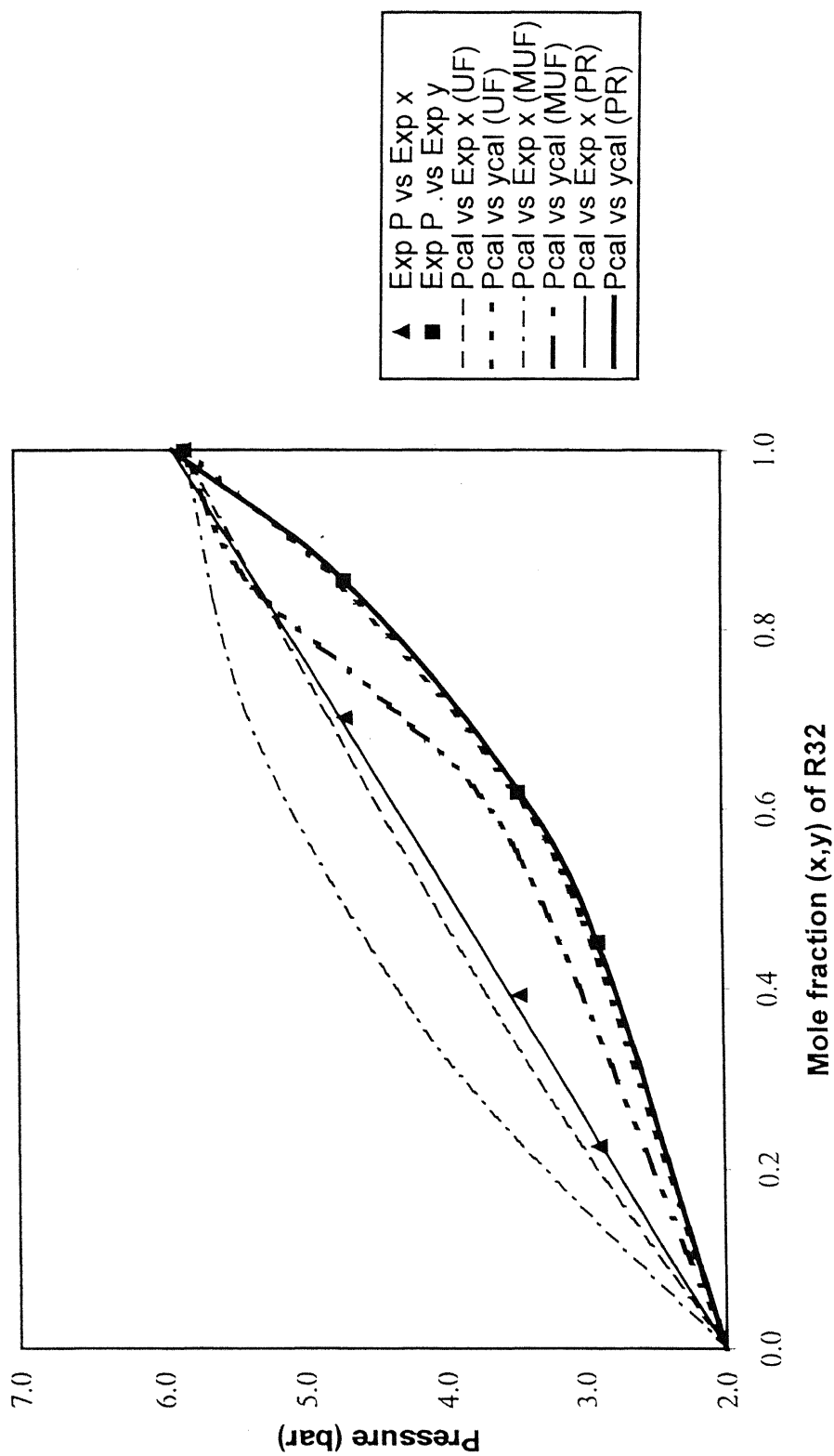


Figure 5.5. P-x-y diagram for R32 (1) / R134a (2) system at T=263.15 K

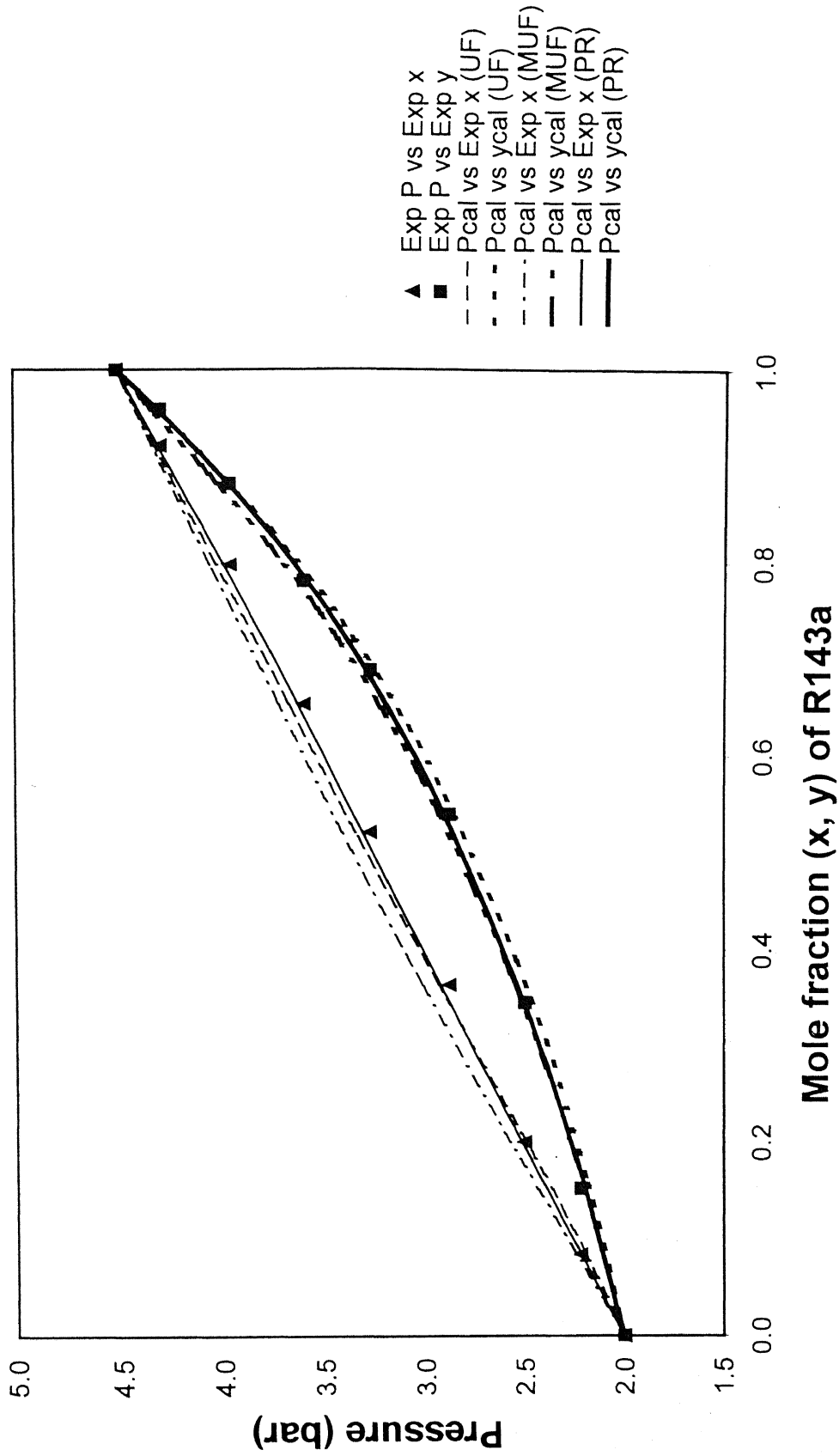


Figure 5.6. P-x-y diagram for R143a (1) / R134a (2) system at  $T=263.15\text{ K}$

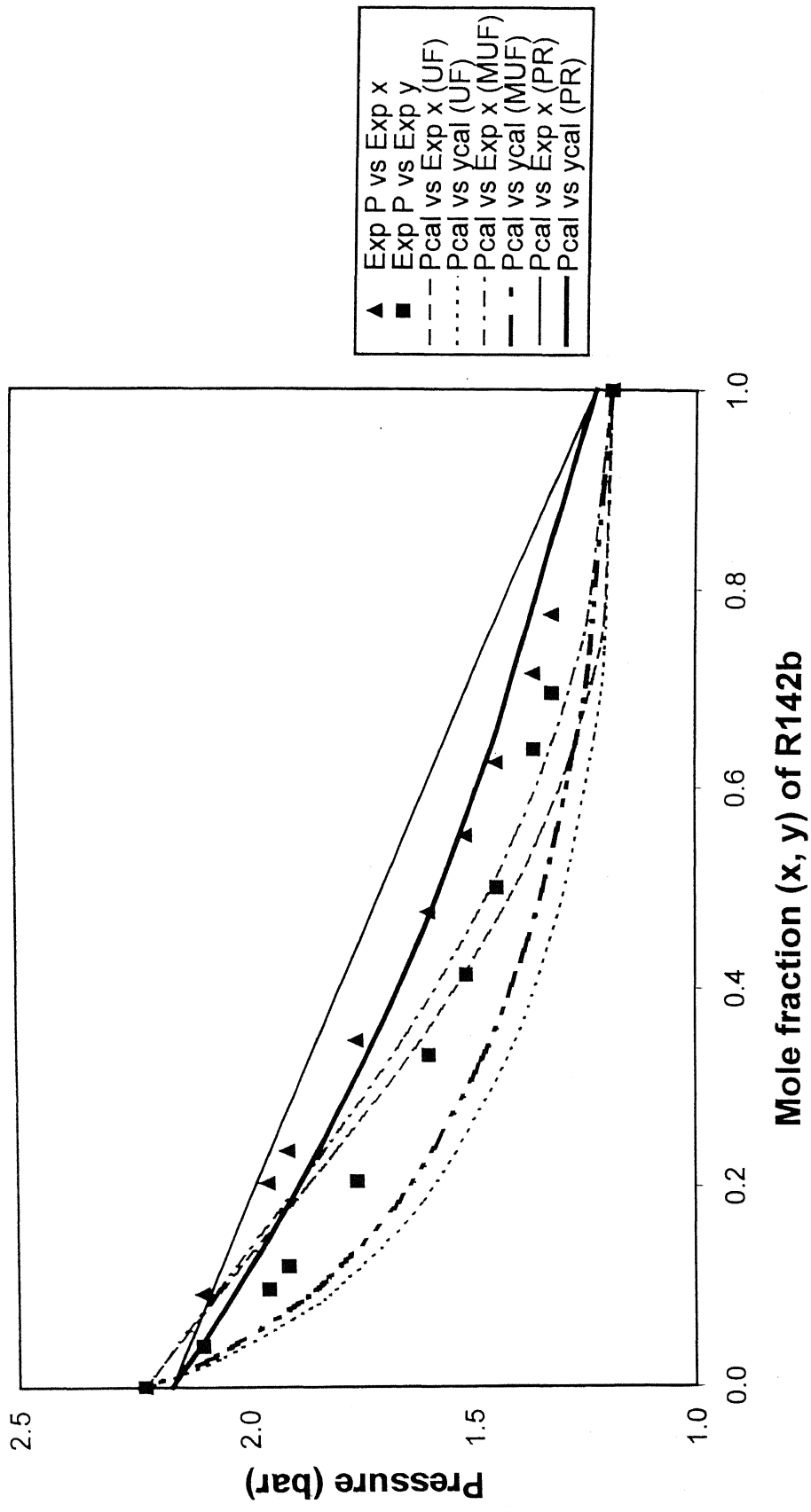


Figure 5.7. P-x-y diagram for R142b (1) / Dimethyl ether (2) system at T=268.0 K

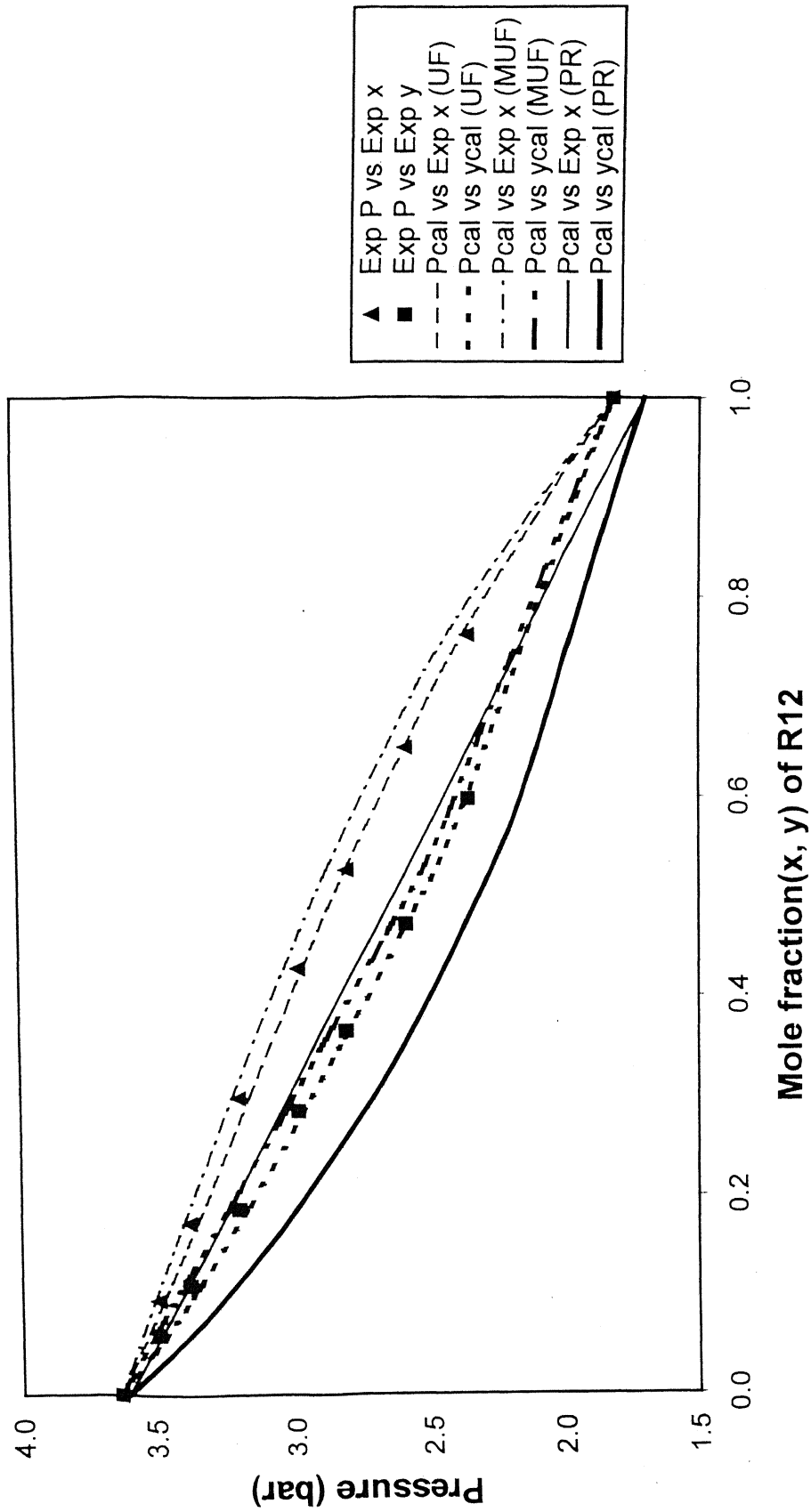


Figure 5.8. P-x-y diagram for Propylene (1) / R12 (2) system at T=258.0 K



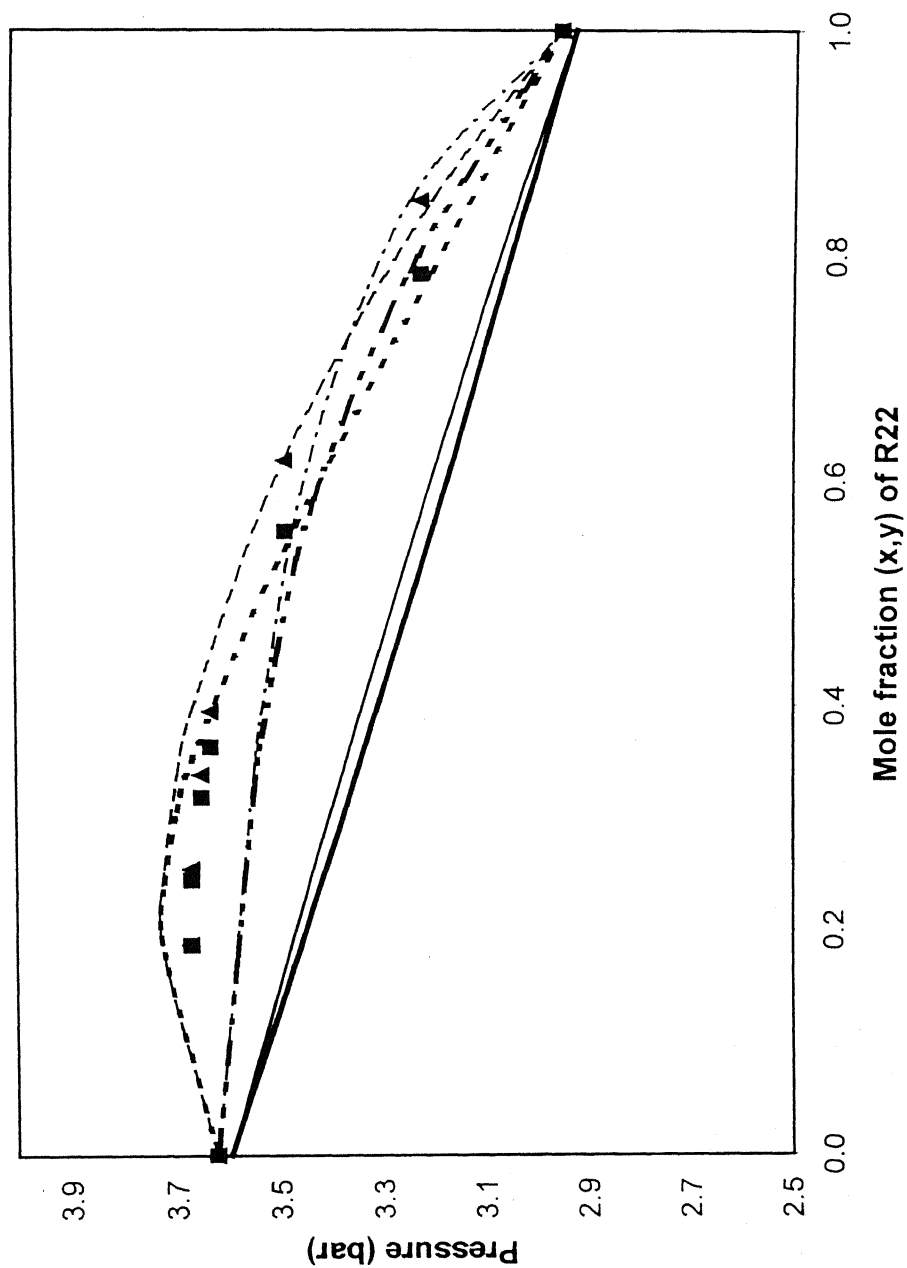


Figure 5.9. P-x-y diagram for propylene (1) / R22 (2) system at T=258.0 K

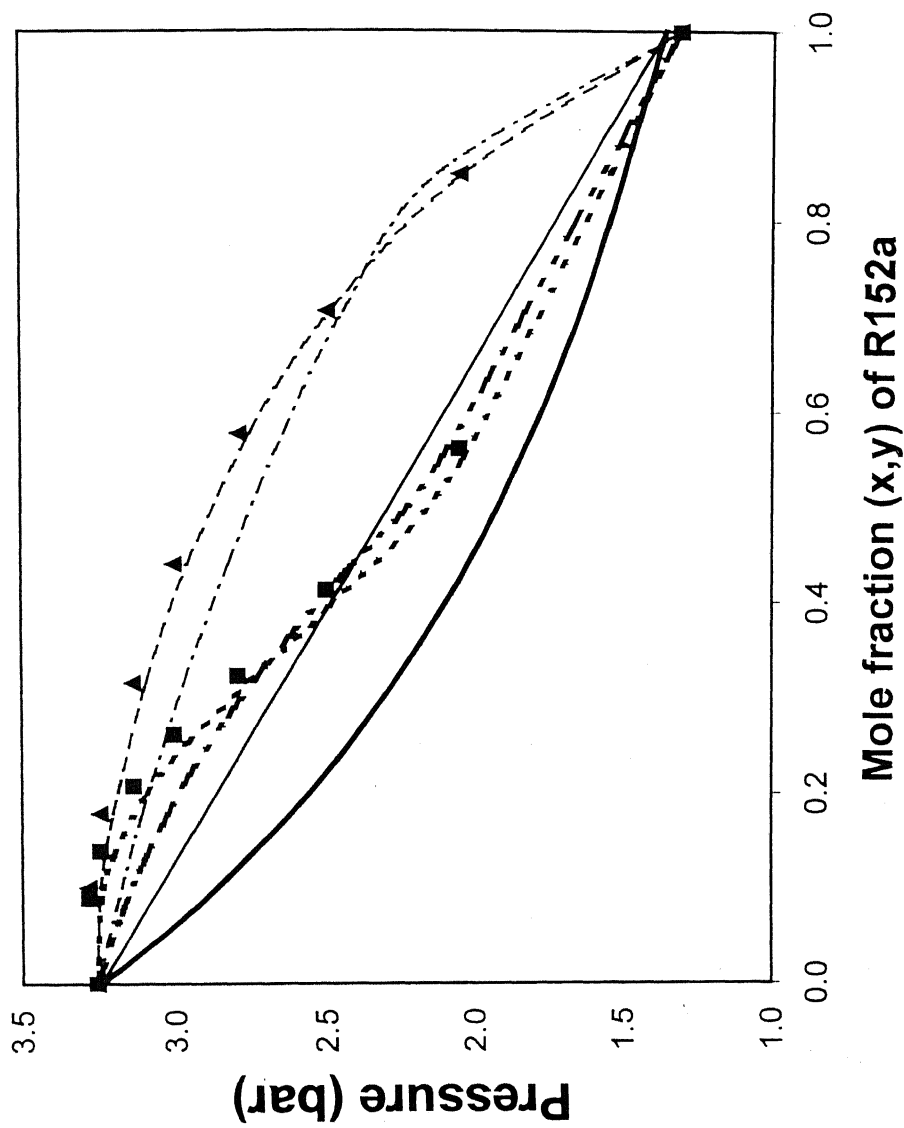


Figure 5.10. P-x-y diagram for Propylene (1) / R152a (2) system at T=255.0 K

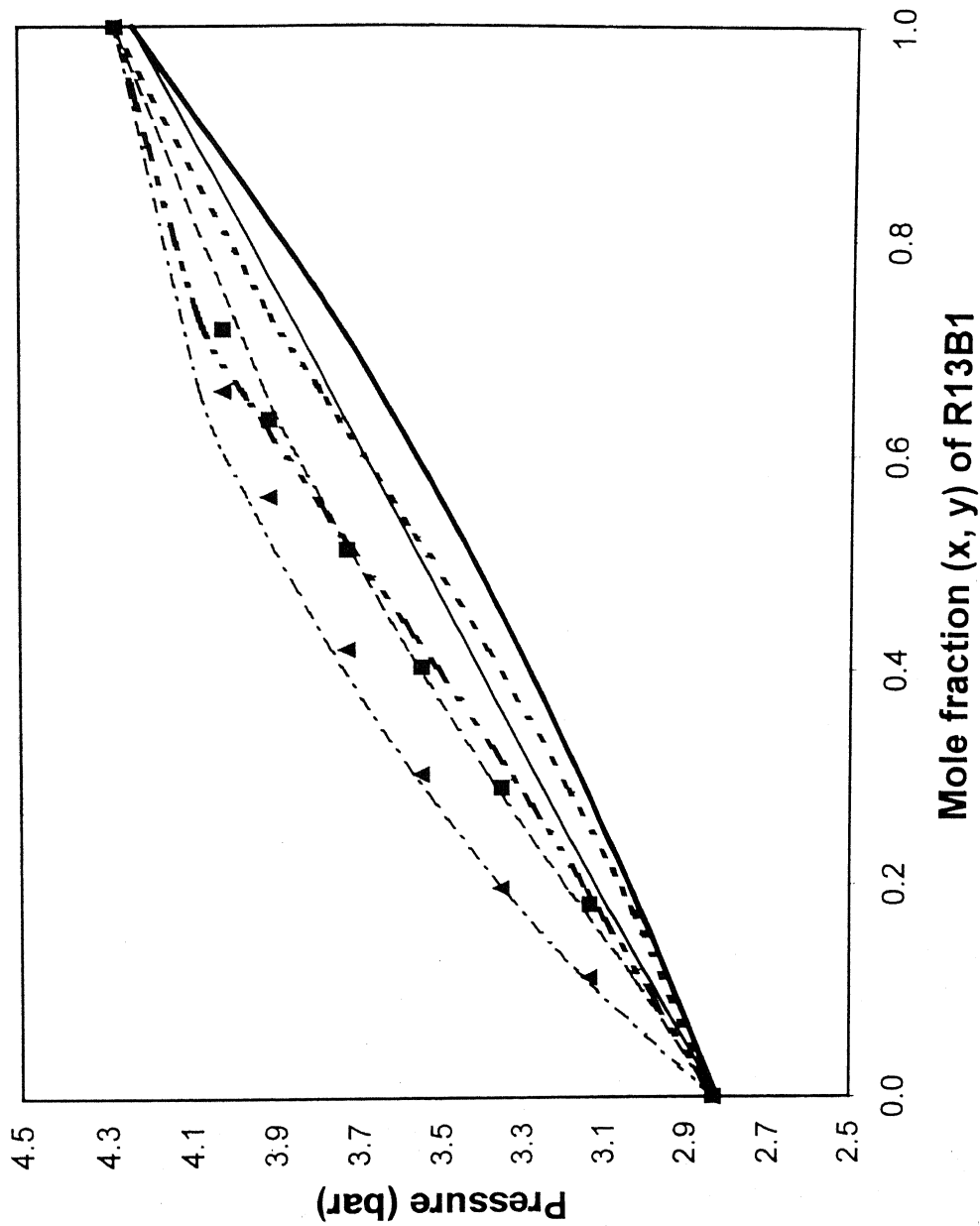


Figure 5.11. P-x-y diagram for Propylene (1) / R13B1 (2) system at  $T = 251.0 \text{ K}$

# CONCLUSIONS

The activity coefficient is directly related to molar Gibbs energy. A total of thirty-one binary mixtures of different classes at different temperatures, have been studied using UNIFAC, modified UNIFAC and Peng-Robinson EOS with van der Waal one fluid mixing rule models and predicted results are compared with experimental data. It was found that the UNIFAC model is able to predict the VLE data much better than the other two models.

For HCFC/HFC, HFC/HFC, BRFC/CFC class of systems and R22-R142b, R134a-R142b systems, the VLE obtained by the P-R with vdW one fluid mixing rule gave better results than other two models. For HFC/HC, HFC/HOC, HCFC/HOC, HC/BrFC class of systems and R134a-R124 system, the VLE data obtained by the Modified UNIFAC method gave better results than other two models.

Further studies can be carried out for the prediction of Vapor-Liquid Equilibria data of a large number of systems using both EOS and Activity coefficient method with different mixing rules.

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